

**THE FATE OF CARBON AND NITROGEN
FROM AN ORGANIC EFFLUENT
IRRIGATED ONTO SOIL – PROCESS STUDIES,
MODEL DEVELOPMENT AND TESTING.**

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The fate of the carbon and nitrogen in dairy farm effluent (DFE) applied onto soil was investigated through laboratory experiments and field lysimeter studies. They resulted in the development and testing of a complex carbon (C) and nitrogen (N) simulation model (CaNS-Eff) of the soil-plant-microbial system.

To minimise the risk of contamination of surface waters, regulatory authorities in New Zealand promote irrigation onto land as the preferred treatment method for DFE. The allowable annual loading rates for DFE, as defined in statutory regional plans, are based on annual N balance calculations, comparing N inputs to outputs from the farming system. Little information is available, however, to assess the effects that these loading rates have on the receiving environment. It is this need, to understand the fate of land-applied DFE and develop a tool to describe the process, that is addressed in this research.

The microbially mediated net N mineralisation from DFE takes a central role in the turnover of DFE, as the total N in DFE is dominated by organic N. In a laboratory experiment, where DFE was applied at the standard farm loading rate of 68 kg N ha⁻¹, the net C mineralisation from the DFE was finished 13 days after application and represented 30% of the applied C, with no net N mineralisation being measured by Day 113. The soluble fraction of DFE appeared to have a microbial availability similar to that of glucose. The low and gradually changing respiration rate measured from DFE indicated a semi-continuous substrate supply to the microbial biomass, reflecting the complex nature and broad range of C compounds in DFE. The repeated application of DFE will gradually enhance the mineralisable fraction of the total soil organic N and in the long term increase net N mineralisation.

To address the lack of data on the fate of faecal-N in DFE, a ¹⁵N-labelled faecal component of DFE was applied under two different water treatments onto intact soil cores with pasture growing on them. At the end of 255 days, approximately 2% of the applied faecal ¹⁵N had been leached, 11% was in plant material, 11% was still as effluent on the surface, and 40% remained in the soil (39% as organic N). Unmeasured gaseous losses and physical losses from the soil surface of the cores supposedly account for the remaining ¹⁵N (approximately 36%). Separate analysis of the total and ammonium nitrogen contents and ¹⁵N enrichments of the DFE and filtered sub-samples (0.5 mm, 0.2 µm) showed that the faecal-N fraction was not labelled homogeneously. Due to this heterogeneity, which was exacerbated by the filtration of DFE on the soil surface, it was difficult to calculate the turnover of the total faecal-N fraction based on ¹⁵N results.

By making a simplifying assumption about the enrichment of the ^{15}N in the DFE that infiltrated the soil, the contribution from DFE-N to all plant available N fractions including soil inorganic N was estimated to have been approximately 11% of the applied DFE-N.

An initial two-year study investigating the feasibility of manipulating soil water conditions through controlled drainage to enhance denitrification from irrigated DFE was extended a further two years for this thesis project. The resulting four-year data set provided the opportunity to evaluate the sustainability of DFE application onto land, an extended data set against which to test the adequacy of CaNS-Eff, and to identify the key processes in the fate of DFE irrigated onto soil under field conditions.

In the final year of DFE irrigation, $1554 \text{ kg N ha}^{-1}$ of DFE-N was applied onto the lysimeters, with the main removal mechanism being pasture uptake ($700 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ removed). An average of $193 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ was leached, with 80% of this being organic N. The nitrate leaching decreased with increasing soil moisture conditions through controlled drainage. At the high DFE loading rate used, the total soil C and N, pH and the microbial biomass increased at different rates over the four years. The long-term sustainability of the application of DFE can only be maintained when the supply of inorganic N is matched by the demand of the pasture.

The complex simulation model (CaNS-Eff) of the soil-plant-microbial system was developed to describe the transport and transformations of C and N components in effluents applied onto the soil. The model addresses the shortcomings in existing models and simulates the transport, adsorption and filtration of both dissolved and particulate components of an effluent. The soil matrix is divided into mobile and immobile flow domains with convective flow of solutes occurring in the mobile fraction only. Diffusion is considered to occur between the micropore and mesopore domains both between and within a soil layer, allowing dissolved material to move into the immobile zone.

To select an appropriate sub-model to simulate the water fluxes within CaNS-Eff, the measured drainage volumes and water table heights from the lysimeters were compared to simulated values over four years. Two different modelling approaches were compared, a simpler water balance model, DRAINMOD, and a solution to Richards' equation, SWIM. Both models provided excellent estimation of the total amount of drainage and water table height. The greatest errors in drainage volume were associated with rain events over the summer and autumn, when antecedent soil conditions were driest. When soil water and interlayer fluxes are required at small time steps such as during infiltration under DFE-irrigation, SWIM's more mechanistic approach offered more flexibility and consequently was the sub-model selected to use within CaNS-Eff.

Measured bromide leaching from the lysimeters showed that on average 18% of the bromide from an irrigation event bypassed the soil matrix and was leached in the initial drainage event. This bypass mechanism accounted for the high amount of organic N leached under DFE-irrigation onto these soils and a description of this bypass process needed to be included in CaNS-Eff.

Between 80 and 90% of the N and C leached from the lysimeters was particulate ($> 0.2 \mu\text{m}$ in size), demonstrating the need to describe transport of particulate material in CaNS-Eff. The filtration behaviour of four soil horizons was measured by characterising the size of C material in a DFE, applying this DFE

onto intact soil cores, and collecting and analyzing the resulting leachate using the same size characterisation. After two water flushes, an average of 34% of the applied DFE-C was leached through the top 0-50 mm soil cores, with a corresponding amount of 27% being leached from the 50-150 mm soil cores. Most of the C leaching occurred during the initial DFE application onto the soil. To simulate the transport and leaching of particulate C, a sub-model was developed and parameterised that describes the movement of the effluent in terms of filtering and trapping the C within a soil horizon and then washing it out with subsequent flow events.

The microbial availability of the various organic fractions within the soil system are described in CaNS-Eff by availability spectra of multiple first-order decay functions. The simulation of microbial dynamics is based on actual consumption of available C for three microbial biomass populations: heterotrophs, nitrifiers and denitrifiers. The respiration level of a population is controlled by the amount of C that is available to that population. This respiration rate can vary between low level maintenance requirements, when very little substrate is available, and higher levels when excess substrate is available to an actively growing population. The plant component is described as both above- and below-ground fractions of a ryegrass-clover pasture.

The parameter set used in CaNS-Eff to simulate the fate of DFE irrigated onto the conventionally drained lysimeter treatments over three years with a subsequent 10-months non-irrigation period was derived from own laboratory studies, field measurements, experimental literature data and published model studies. As no systematic calibration exercise was undertaken to optimise these parameters, the parameter set should be considered as “initial best estimates” and not as a calibrated data set on which a full validation of CaNS-Eff could be based.

Over the 42 months of simulation, the cumulative drainage from CaNS-Eff for the conventionally drained DFE lysimeter was always within the 95% CI of the measured value. On the basis of individual drainage bulking periods, CaNS-Eff was able to explain 92% of the variation in the measured drainage volumes. On an event basis the accuracy of the simulated water filled pore space (WFPS) was better than that of the drainage volume, with an average of 70% of the simulated WFPS values being within the 95% CI for the soil layers investigated, compared to 44% for the drainage volumes. Overall the hydrological component of CaNS-Eff, which is based on the SWIM model, could be considered as satisfactory for the purposes of predicting the soil water status and drainage volume from the conventionally drained lysimeter treatment for this study.

The simulated cumulative nitrate leaching of $4.7 \text{ g NO}_3\text{-N m}^{-2}$ over the 42 months of lysimeter operation was in good agreement to the measured amount of $3.0 (\pm 2.7) \text{ g NO}_3\text{-N m}^{-2}$. Similarly, the total simulated ammonium leaching of $2.7 \text{ g NH}_4\text{-N m}^{-2}$ was very close to the measured amount of $2.5 (\pm 1.35) \text{ g NH}_4\text{-N m}^{-2}$, however the dynamics were not as close to the measured values as with the nitrate leaching. The simulated amount of organic N leached was approximately double that measured, and most of the difference originated from the simulated de-adsorption of the dissolved fraction of organic N during the 10-month period after the final DFE irrigation. The 305 g C m^{-2} of simulated particulate C leached was close to the measured amount of 224 g C m^{-2} over the 31 months of simulation. The dissolved C fraction was substantially over-predicted. There was good agreement in the non-adsorbed and particulate fractions

of the leached C and N in DFE. However, the isothermic behaviour of the adsorbed pools indicated that a non-reversible component needed to be introduced or that the dynamics of the de-adsorption needed to be improved. Taking into account that the parameters were not calibrated but only “initial best estimates”, the agreement in the dynamics and the absolute amounts between the measured and simulated values of leached C and N demonstrated that CaNS-Eff contains an adequate description of the leaching processes following DFE irrigation onto the soil.

The simulated pasture N production was in reasonable agreement with the measured data. The simulated dynamics and amounts of microbial biomass in the topsoil layers were in good agreement with the measured data. This is an important result as the soil microbial biomass is the key transformation station for organic materials. Excepting the topsoil layer, the simulated total C and N dynamics were close to the measured values. The model predicted an accumulation of C and N in the topsoil layer as expected, but not measured. Although no measurements were available to compare the dynamics and amounts of the soil $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$, the simulated values appear realistic for an effluent treatment site and are consistent with measured pasture data.

Considering the large amount of total N and C applied onto the lysimeters over the 42 months of operation (4 t ha^{-1} of N and 42 t ha^{-1} of C), the various forms of C and N in dissolved and particulate DFE as well as in returned pasture, and that the parameters used in the test have not been calibrated, the simulated values from CaNS-Eff compared satisfactorily to the measured data.

Keywords: Carbon, nitrogen, organic effluent, nitrate leaching, dairy farm effluent (DFE), soil-plant-microbial system, mineralisation, immobilisation, microbial biomass, faecal ^{15}N , controlled drainage, lysimeters, bypass flow, simulation model, multiple availability spectrum, dissolved and particulate organic matter, filtration, mobile and immobile flow domains, diffusion, non-equilibrium adsorption-desorption kinetics.

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Chapter One

Introduction

1.1 Background

With the increasing pressure on the environment the careful use and management of our natural resources are of paramount importance. For activities which are based around the use of natural resources, the balance between profitable operation and environmental sustainability must be carefully maintained. In New Zealand, activities such as agricultural and horticultural production and land-based waste treatment must not only function economically but must also maintain a healthy environment.

The legislative framework in New Zealand for the management and sustainable use of natural resources is the Resource Management Act (RMA) (MfE, 1991). This legislation promulgates an effects-based approach to the consent process to allow the use of natural resources as opposed to prescriptive or standards-based criteria. With an approach such as this, the emphasis is on predicting the likely environmental effects that a proposed activity would have on the receiving environment, such as ground or surface waterways. For farming or land-based waste treatment the environmental impacts are a function of the complex inter-related physical, chemical and biological processes that occur within the soil-plant system. The assessment of these impacts as required by the RMA would be greatly simplified if comprehensive and well-tested predictive tools were available.

1.2 Land-based waste treatment

Over the last ten years there has been a significant movement in New Zealand towards the land treatment of wastes. This has been driven by a number of factors including the recognition that the discharge of effluents into surface waterways has been degrading water quality and that much of the material being discharged was actually a valuable plant nutrient source. Also, the indigenous people of New Zealand find the practice of discharging treated or untreated wastes directly into surface waterways offensive and unacceptable. These factors resulted in the RMA legislation being adopted in 1991. This Act requires any proposed waste treatment system to consider the feasibility of using a land-based treatment system.

One of the major waste streams of the largest industry in New Zealand, the dairy industry, comes from the cleaning of the milking dairy and associated holding yards on the farm. This very dilute organic effluent, called dairy farm effluent (DFE), consists of a mixture of urine and faeces combined with wash down water. The daily volume of DFE produced by an average New Zealand dairy farm is equivalent, on a biological oxygen demand (BOD) basis, to the sewage of over 700 people, based on data from LIC (1995) and Dakers and Painter (1982). In terms of total nitrogen (N) loading, it is equivalent to a population of over 200 people. With the reticulation of individual farms for effluent collection being impractical, and dairy cow numbers increasing by 57% over the last 20 years (LIC, 1995), the regulatory bodies have responded by promoting application of DFE onto land as their preferred treatment option. The adoption of this technology has been relatively rapid. In the Waikato, a major dairying region of New Zealand, the proportion of farmers who treat DFE by applying it to land has doubled from 35% to nearly 70% between 1993 and 1997 (Selvarajah, 1998).

However, land application needs to be treated somewhat as a “Pandora’s box” with groundwater nitrate levels already being elevated under intensively farmed areas (Burden, 1982; Hoare, 1986; Smith *et al.*, 1993) and the risk of inappropriately managed DFE irrigation further exacerbating groundwater nitrate levels. The allowable annual loading rates for DFE, as defined in statutory regional plans for various regions of New Zealand, range from 100 to 300 kg N ha⁻¹ yr⁻¹. These rates are largely based on annual N balance calculations comparing typical N loading inputs to outputs within the farming system, which include an allowable leaching loss (e.g. Selvarajah, 1996). Little information is available however to assess the effects that these loading rates have on the receiving environment (Selvarajah, 1996; Longhurst *et al.*, 1999).

Computer simulation tools which have the ability to integrate the complex and varied transport, transformation and uptake processes that govern the fate of surface-applied materials are the only realistic technique to assess such effects. In recent years, there has been considerable growth in this area with the knowledge from different disciplines being combined into more holistic descriptions. This trend in part can be attributed to the increasing availability of relatively sophisticated computing hardware. These types of mathematical models are well suited to addressing environmental problems, which generally have a large number of complex dependent relationships that require integrating in a holistic manner. This integration is a prerequisite for making confident predictions of the impacts from perturbations or changes to the natural systems. Simulation tools also offer the capability to run scenarios over a wide range of management alternatives for both short and longer time periods, thus making these tools extremely attractive and useful to the managers of natural resources.

It is the need to better understand the fate of land-applied DFE and to develop a predictive tool to describe this process that is addressed in this thesis. This goal is met through a combination of laboratory experiments and field studies, which have resulted in the development and testing of a simulation model (CaNS-Eff), capable of describing the fate of DFE applied onto land.

1.3 The goal and objectives of the study

The overall goal of the research reported in this thesis was to:

Understand the fate of land-applied DFE and develop a tool capable of simulating this treatment process.

This goal was met through the following objectives:

1. Identify and understand the key processes that control the fate of DFE irrigated onto soil.
2. Develop a mathematical description for these processes and integrate them into a holistic model.
3. Determine parameters that are suitable for use in the mathematical descriptions.
4. Develop data sets that can be used to test the model.
5. Check the adequacy of the model by comparing simulated values against measured data.

To address these objectives four separate facets of work were undertaken.

1. Laboratory process studies have been completed to:
 - Obtain an understanding of the soil biological processes involved when organic material is added to the soil.
 - Determine parameters that describe the response of microbial biomass populations when organic material is added to soil.
 - Describe and parameterise the transport of the particulate fraction of DFE in soil.
 - Describe the non-equilibrium adsorption kinetics involved in the addition of DFE to soil.
2. Field lysimeter studies were used to:
 - Identify key processes in the fate of organic effluent irrigated onto soils under field conditions.
 - Provide data sets to test the simulation model.
3. The development and parameterisation of a comprehensive simulation model (CaNS-Eff) describing the fate of organic effluent added to soil.
4. The comparison of simulated values from CaNS-Eff with measured data to ascertain the adequacy of the model to describe the fate of DFE irrigated onto soil.

1.4 Thesis layout

The thesis is divided into six sections, with a number of Chapters contributing to each of the sections, as shown in Table 1.1. Five of the fifteen Chapters are refereed published papers with another Chapter being from a published conference proceedings. The way in which the sections fit together to form the complete study is shown in Figure 1.1.

Table 1.1 Contents of each section within this thesis.

Section	Chapters
1. Introduction and literature review	1 and 2
2. Laboratory process studies	3 to 6
3. Results of field lysimeters	7 and 8
4. Model development and parameterisation	9 to 11
5. Testing of the simulation model	12 to 14
6. Summary	15

The laboratories and field studies provided an understanding of the processes that are important in describing the fate of DFE irrigated onto soil. The laboratory studies have also been used to assist in parameterising equations used in the model to describe the relevant processes. The model uses a combination of techniques from existing models and new descriptions for processes either not previously modelled or where improved descriptions have been proposed. The four years of field data have then been used to compare the simulated values with CaNS-Eff.

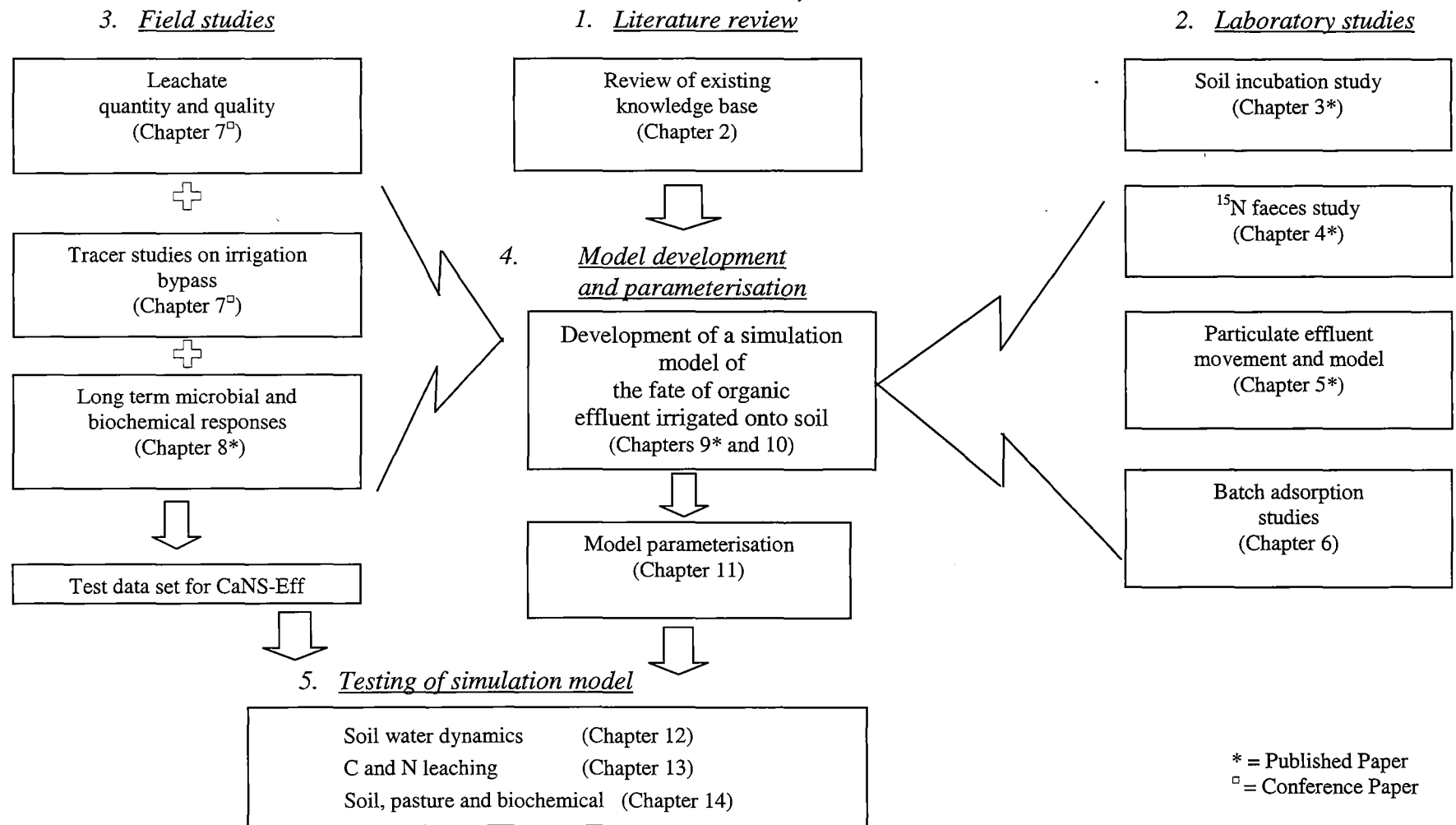


Figure 1.1 Outline of thesis. Chapter 1 (Introduction) and Chapter 15 (Summary) not shown.

1.5 Laboratory process studies

The function and contribution of each of the four laboratory studies to the overall project are briefly outlined below.

Chapter 3: Immobilisation and mineralisation of C and N from DFE during laboratory incubations

This study was undertaken to obtain information on the mineralisation of C and N when DFE is added to the soil. The incorporation into microbial biomass from the two fractions (soluble and particulate) of DFE at two loading rates was investigated and the mineralisation rates from DFE were compared against soluble sources of C and N (glucose and ammonium).

Chapter 4: Fate of the ^{15}N -labelled faeces fraction of DFE irrigated onto soils under different water regimes

Whereas the dynamics of the urine fraction are comparatively well understood, there is a lack of data on the fate of the mainly organic faecal fraction in DFE. To improve the understanding of the complex turnover processes, both the inorganic and organic N compounds of the faecal fraction of DFE were labelled with ^{15}N . The N dynamics were then measured in various soil and plant fractions in two water content treatments in lysimeters under laboratory conditions for 254 days.

Chapter 5: Leaching of particulate organic C from land-applied DFE

A detailed investigation into the leaching behaviour of the particulate fraction of DFE applied onto a poorly drained soil is presented in this Chapter. The study entailed dividing the particulate fraction of DFE into a number of arbitrary size-classes and determining the amounts of organic C present in each of these classes by physical filtration and subsequent C measurement. The filtration characteristics of each of the soil horizons were determined by differences between the C in the applied effluent and that leached through soil cores for each of the size-classes.

A simulation model that describes the transport in soil of particulate organic material contained in DFE is also presented and parameterised.

Chapter 6: The adsorption kinetics of ammonium and dissolved organic fractions of DFE added to soil

The adsorption characteristics of the dissolved C and ammonium fractions of DFE in various soil horizons have been determined using batch equilibrium studies. A non-equilibrium model based on the principles of the Langmuir adsorption equation is presented. Parameters are derived from the batch studies to describe this non-equilibrium adsorption behaviour of the dissolved fractions of DFE.

1.6 Field lysimeter study

The field lysimeter study involved the irrigation of fresh DFE onto large lysimeters (60 cm dia.) over three years with subsequent monitoring for a fourth year when no DFE was applied. This field study was part of a larger project initiated to investigate the feasibility of promoting denitrification by manipulating soil water conditions to enhance nitrate removal from land-applied DFE. The control of the soil water conditions was achieved using a technique called controlled drainage. The quantity and quality of leachate as well as pasture uptake and changes in soil biochemical parameters were measured over the four years of operation. The leachate quality and denitrification measurements from the lysimeters over the first two years are not considered part of this thesis as these were the responsibility of a colleague who has reported these results separately (Singleton, 1997; Singleton *et al.*, 2001).

There are two Chapters which discuss the relevant results from the field lysimeters.

Chapter 7: Impact of controlled drainage on N leaching and solute behaviour

The leachate quantity and quality as well as pasture uptake results for the third year of operation of the lysimeters are presented in this Chapter. These measurements are compared with the simulated values in the model testing section of the project. Bromide tracer results are also presented which showed that leachate quality is dominated by the initial bypass flow event and then a slow release from the immobile soil water zone. This bypass behaviour was the dominant feature of the application of DFE onto this soil and had a major influence on the development of CaNS-Eff.

Chapter 8: Effects of regular irrigation with DFE on soil organic matter and soil microbial biomass

This Chapter reports on the rate at which the resistant organic matter from DFE accumulates in the soil in organic C and total N and the effect of this accumulation on other soil organic matter (SOM) related pools such as microbial biomass. These changes over the four years of operation of the lysimeters determine the long-term impact and sustainability of land-applied DFE. These measurements form part of a data set against which the predictions from CaNS-Eff are tested.

1.7 Model development and parameterisation

There are two Chapters (Chapters 9 and 10) that discuss the development of the complex C and N soil-plant-microbial model CaNS-Eff, and a third Chapter (Chapter 11) describing the parameterisation of the model. Chapter 9 discusses the selection of an appropriate water flux sub-model to use with CaNS-Eff while Chapter 10 discusses in detail the processes that are modelled in CaNS-Eff.

Chapter 9: Hydrology models DRAINMOD and SWIM applied to large soil lysimeters with artificial drainage

This Chapter discusses the comparison of two soil hydrological models, DRAINMOD and SWIM, capable of providing the soil water content and water flux data for CaNS-Eff. The simulated drainage volumes and water table heights are compared to measured values over four years for the three drainage treatments in the lysimeters. The hydrological model that was used with CaNS-Eff was chosen on the basis of this study.

Chapter 10: CaNS-Eff: A Carbon and Nitrogen Simulation model capable of describing the fate of Dairy Farm Effluent applied onto the land

This Chapter provides a detailed description of CaNS-Eff, a model capable of describing the fate of C and N in organic effluents applied onto the land. Components of the model, the linkages between the components, and the operation of the model are discussed.

Chapter 11: Parameterisation of CaNS-Eff to describe the fate of DFE applied onto the land

A discussion of the derivation of the parameter set chosen to use with CaNS-Eff to simulate the fate of C and N from DFE applied onto the conventionally drained lysimeter over the four years of operation.

1.8 Model testing

There are three Chapters that discuss aspects of the testing of the CaNS-Eff simulation model against measured data.

Chapter 12: Soil water dynamics: simulated versus measured

The measured leachate volumes and soil water contents for the conventionally drained lysimeter treatment are compared with the simulated values from CaNS-Eff. This comparison is over 42-months for the drainage data and 29-months for the soil water contents. The goodness of fit of the simulated values, both on a cumulative and event basis, are discussed.

Chapter 13: C and N leaching: simulated versus measured

Simulated N and C leaching amounts in various organic and inorganic forms are compared to measured weekly replicated data from the conventionally drained lysimeter over a 42-month period for the N and 31-months for the C. The simulated versus measured leachate quality on a cumulative basis for the various fractions is analysed.

Chapter 14: Pasture, microbial biomass and soil C and N response: simulated versus measured

This Chapter reports on the performance of CaNS-Eff in terms of the plant, microbial biomass and soil C and N levels, by comparing the simulated and measured values for pasture N uptake and for the 0-5, 5-10 and 10-20 cm soil layers the microbial biomass and total soil C and N concentrations. The inorganic soil N concentrations in the same three soil layers are also reported but no measured data were available for comparison.

1.9 Author's declaration

The author has been the principal research engineer who has undertaken or been responsible for the planning, development and implementation of the experimental design, the measurement, results, write-up and the model development and testing contained in this thesis, except for:

1. The writing and implementation of the code for the CaNS-Eff model.
2. The results from the DFE-irrigated lysimeter experiment during the first two years of operation.

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Chapter Two

Review of literature on the fate of DFE applied onto soils and simulation models capable of describing the addition of organic amendments to soil

The objectives of this Chapter are to review and summarise published information on:

Field and laboratory studies describing the effects and fate of C and N in DFE applied onto soils

Simulation models and techniques previously used or capable of describing the C and N dynamics when organic effluents are added to soil

2.1 DFE studies

2.1.1 Characteristics of DFE

DFE is created when the milking equipment, the dairy parlour floor and the associated holding yards are washed with large volumes of water after each milking. This operation results in a very dilute mixture of faeces, urine and water. The mean total solids and N characteristics of DFE are given in Table 2.1 based on a review by Longhurst *et al.* (2000) of 11 published studies. This work shows that the dominant form of N in DFE is organic N.

Most of this organic N comes from the faeces, which consist of undigested dietary constituents and microbial cells and their residues, plus cells and enzyme residues from the animal’s digestive system. Chemically, these nitrogenous compounds are made up of 45-65% amino N, about 5% nucleic acids, with the remainder consisting of partially degraded nucleic acids, bacteria cell walls and glycoprotein, and N bound to fibre (Whitehead, 1995). In fresh urine 60-90% of the total N is urea, which is rapidly hydrolysed to ammonium in DFE.

Table 2.1 Mean concentrations of total solids, N fractions within DFE (sample size = 37), source Longhurst *et al.* (2000).

Characteristic	%	mg N l ⁻¹	% of total N
Total solids	0.90	—	—
Total N	—	400	—
Organic N	—	324	81
Ammonium-N	—	72	18
Nitrate-N	—	2	2

Biological and chemical oxygen demand of DFE have been reported by Cooke *et al.* (1979) and Vanderholm (1984) with total C contents measured by Di *et al.* (1998a) as given in Table 2.2.

Table 2.2 Oxygen demand and C characteristics of DFE.

Characteristic	mg O ₂ l ⁻¹	mg C l ⁻¹
BOD ₅ (Cooke <i>et al.</i> , 1979)	3825	—
(Vanderholm, 1984)	1500	—
COD (Cooke <i>et al.</i> , 1979)	8560	—
(Vanderholm, 1984)	6600	—
Total C (Di <i>et al.</i> , 1998a)	—	700 to 6500

2.2 Fate of organic materials applied onto the soil

DFE is typically applied daily onto grazed ryegrass-clover pasture with up to six applications on the same area in a year. The characteristics of DFE and the regular daily application mean that results from overseas studies using stored slurries with higher solids and ammonium contents and applications only once a year are not comparable to DFE results. For this reason, this review has focused on DFE studies undertaken under New Zealand conditions.

It is not the intention of this literature review to describe the soil N cycle in detail. However, as organic N dominates DFE, it is appropriate to briefly discuss what occurs when organic materials are added to the soil. While the regulatory emphasis is on the fate of N in DFE it is important to realise that it is the C fraction which is the driving factor in the dynamics of organic materials added to the soil.

Organic materials added to soil are either dead plant materials such as leaf litter or dead roots, excreta of farm animals or dead soil organisms such as fungi, bacteria and nematodes. These organic materials are made from simple compounds such as sugars, starches, amino acids and proteins through to cellulose, hemi-cellulose, lignin and more complex phenols, fats and waxes (Smith, 1982). Organic compounds are generally made up of carbon, hydrogen, oxygen, nitrogen, sulphur and phosphorous which are bound together differently so as to give each compound a unique function or property within the organic material.

When the organic material is added to soil the C fraction of the material becomes a substrate for the soil microorganisms. They utilise this C as an energy source and for microbial growth (Paul and Clark, 1989). Depending on the nutrient status of the microorganisms, other nutrients such as N or P may also be consumed (immobilised) or remain extra-cellular which makes the nutrient available for other soil processes (net mineralisation). There are two microbial pathways which use the C. The first is respiration to fulfil the energy requirements of the soil microorganism. In this process, the C is oxidised under aerobic conditions and released as carbon dioxide (CO_2). In the second pathway the C is used for maintenance or growth of the biomass itself and so the C is incorporated into the soil biomass (C_{mic}) (Paul and van Veen, 1979; van Veen *et al.*, 1984). Under anaerobic conditions different soil microorganisms will consume the C in the respiration process and produce only partly oxidised products such as methane (CH_4) or ethylene (C_2H_2) instead of CO_2 .

In the process of using the organic material the soil organisms may also produce excretion products which can be substrates for other microorganisms. When microorganisms themselves die, either due to substrate depletion or unfavourable environmental conditions, they also become a substrate for other microorganisms and part of the mineralisation-immobilisation-turnover (MIT) (Jansson and Persson, 1982). In the degradation process, the organic material may also form other by-products or metabolites which can be quite resistant to breakdown and contribute to the soil humus pool (humification) (McLaren and Cameron, 1990). Obviously, the organic material that is the easiest to break down or consume will be used by the soil microorganisms first, with the more resistant material remaining longer in the soil. Different types of microorganisms are better adapted to consuming different organic materials and so changes in the make-up of the active microbial population will reflect the type of substrate that is present

in the soil. The actual rate at which the decomposition process occurs depends on many environmental factors including temperature, soil water content, clay content and soil acidity as well as the ability of the biomass to use the C in the organic material. The prediction of the fate of animal manures is particularly complex because of the variable products that make up the material and the poorly understood interactions between large inorganic and organic pools (Shepherd *et al.*, 1996).

In DFE, where most of the N is in the form of organic N, the C:N ratio of the biomass and the organic material being degraded influences the amount of N that is either directly mineralised as NH_4 or immobilised into microbial-N fractions. The immobilised N can be subsequently mineralised or re-immobilised when the biomass dies. Some of the organic N can also be associated with highly resistant organic fractions within the DFE which may be microbially unavailable. While the release of N from organic materials can be described qualitatively, there is a poor understanding of the pools in which N is contained within the manures, the rate at which it is released and the interactions between pools. Thomsen *et al.* (1997) stressed that, in order to be able to predict more accurately the fate of N contained in animal manures, more information on the mineralisation rates from the organic manure fraction and remineralisation of immobilised N was urgently required.

2.3 DFE leaching and pasture response studies

Field studies involving DFE applied onto pasture have generally been undertaken for two purposes: firstly to investigate the pasture response due to the DFE application, and secondly to measure the environmental impact in terms of changes in the quality of leachate from DFE applications. Not all investigations have measured both components.

The first published study on the effect of DFE on the leachate composition from DFE-irrigated pasture was by Macgregor *et al.* (1979). The soil was a mole and tile drained silt loam under grazed dairy management. Of the annual loading of $1125 \text{ kg N ha}^{-1}$ and 125 kg P ha^{-1} applied as DFE, 150 kg N ha^{-1} and 1.6 kg P ha^{-1} were estimated to be lost in drainage waters. In a nearby control plot under pasture, the equivalent N and P losses were 30 kg N ha^{-1} and 0.1 kg P ha^{-1} .

Whereas the predominant form of N leached in the winter drainage waters was NO_3 , in the spring drainage it was dominated by organic N and NH_4 . During spring drainage flow, faecal coliform bacteria and urea were in high concentrations, further indicating that bypass flow can occur when a dilute effluent such as DFE is applied onto drained silt loam soils.

The composition of the drainage waters from the same site was further investigated in a more intensive manner by Cooke *et al.* (1979). While their objective was to establish correct sampling protocols of the drainage flow, the study gave good information on the composition of the drainage waters. They found the ratio of chemical to biological oxygen demand in the drainage waters was high (1.9-2.1), indicating that a large proportion of the organic material in the drainage waters was not biologically oxidisable in five days. The drainage composition results showed that between 65% and 76% of the N in the drainage waters was in an organic form, which agreed with the earlier work by Macgregor *et al.* (1979). They further analysed this organic fraction and found that 18% and 40% for the two drainage events was particulate organic N,

the ammonium fraction was approximately 20% of the total N, with nitrate only being 17% and 4% respectively. The soil-plant system at this site removed approximately 80% of the total N, total P, and BOD₅ that was applied.

Three years of soil and drainage data from this same site were subsequently reported by Macgregor *et al.* (1982). Approximately 280 kg N ha⁻¹ and 18 kg P ha⁻¹ of the 2880-3840 kg N ha⁻¹ and 390-540 kg P ha⁻¹ applied as DFE were leached in drainage waters. The measured P recovery over the three years was close to 95%, with the major part being P accumulation in the soil. In comparison, the N recovery was less than 15%. The authors speculated that gaseous pathways such as denitrification could have been a major loss mechanism for the N. The inability to measure where the applied DFE-N was in the soil-plant system highlighted the lack of information on the fate of land-applied DFE. In early summer the soil inorganic N levels were significantly higher in the DFE treatment compared to the control, but in the autumn and winter samplings they were not significantly different, which gave little clue as to what happened to the large quantities of N applied in the DFE.

In the first study which investigated herbage response, Goold (1980) applied DFE at two loading rates, 156 and 312 kg N ha⁻¹ yr⁻¹, over four milking seasons, onto a Waikare clay soil. The higher DFE loading increased mean annual herbage yield by 43%, with the lower rate increasing yield by 27% over the water-irrigated control. The increase in yield was attributed to the nutrient component of the DFE, as the irrigated control had no increase in herbage yield. The botanical composition of the herbage remained basically stable in all treatments. The author assumed that 88% of the total N applied in DFE was equivalent to fertiliser N, and this resulted in the mean annual herbage yield responses of 16.0 and 26.0 kg DM kg N⁻¹ applied for the low and high DFE treatments respectively. These response rates are similar to other published fertiliser response values for these soils.

As part of a study assessing the environmental effects of dairy farming, the cumulative effects of cow urine, DFE and N fertiliser on NO₃ leaching were investigated by Silva *et al.* (1999). DFE was applied at two loading rates, 200 and 400 kg N ha⁻¹ yr⁻¹, onto undisturbed soil lysimeters of Templeton fine sandy loam. The applications were applied quarterly, and pasture was cut and removed on a regular basis. The NO₃ leaching was 6.3 kg N ha⁻¹ yr⁻¹ (3.2% of applied) from the 200 kg N ha⁻¹ yr⁻¹ treatment and 10.0 kg N ha⁻¹ yr⁻¹ (2.5% of applied) for the 400 kg N ha⁻¹ yr⁻¹. These leaching losses were lower than the 8.3% reported by Macgregor *et al.* (1982). However, it is difficult to make a direct comparison as in the work reported by Silva *et al.* (1999) the loading rates were lower, only NO₃ was measured, and the pasture was managed as a cut and carry system.

In response to the proliferation of dairy farming on irrigated land in the South Island of New Zealand, an investigation into the inorganic N leaching from DFE and inorganic fertiliser (NH₄Cl) under two different irrigation methods, flood and spray, was undertaken by Di *et al.* (1998b). DFE and NH₄Cl in a dissolved form were applied at a loading rate of 400 kg N ha⁻¹ yr⁻¹. The spray irrigated treatments received 50 mm per month of clean water irrigation over the summer period (300 mm total) while the flood irrigated treatments had twice the depth applied. The spray irrigated treatments had 2.8, 25.6 and 49.0 kg inorganic N ha⁻¹ yr⁻¹ leached from the control, DFE and N fertiliser treatments, respectively, while the flood irrigated treatment had 2.6, 13.1 and 47.1 kg inorganic N ha⁻¹, respectively. The N leaching losses in the DFE

treatments represented 6.4 and 3.2% of the applied DFE-N in the spray and flood irrigated treatments, respectively. The lower N leaching losses in the DFE treatments compared to the inorganic fertiliser were attributed to lower amounts of inorganic N and a higher potential for denitrification in the DFE treatment.

The second year's results from the same work (Di *et al.*, 1998a) showed similar results with significantly lower NO₃ leaching losses occurring in the DFE treatments (8-25 kg NO₃-N ha⁻¹) than in the NH₄Cl treatments (28-48 kg NO₃-N ha⁻¹). Over the two-year period the inorganic N leached in the DFE treatments was lower in the flood (25 kg N ha⁻¹) than the spray irrigated (37 kg N ha⁻¹) treatments, which the authors attributed to greater denitrification in the wetter flood irrigated treatment.

The DFE was able to sustain the same amount of herbage production as the NH₄Cl over the two-year period. The N removal by pasture was significantly different between the fertiliser treatments in the second year of the flooded treatment, with the DFE pasture removing 412 kg N ha⁻¹ yr⁻¹ compared to 340 kg N ha⁻¹ yr⁻¹ in the NH₄Cl treatment. There was a change in pasture species with the fertiliser application. The controls had up to 60% clover in the pasture, while the DFE treatment was lower with between 25-40% and the NH₄Cl treatment had only 5-10%.

Ammonia volatilisation from DFE does not appear to be a major loss pathway with measured volatilisation after DFE application only representing 0.05-0.3% of total N applied (i.e. 0.2-1.2% of NH₄).

A further field study involving six loading rates of DFE ranging from 0 to 375 kg N ha⁻¹ in 75 kg N increments applied onto a freely draining Horotiu sandy loam under a cut and carry pasture management was reported by Longhurst *et al.* (1999). Over the 18-month period after application they found that the pasture responses were 7, 15, 15, 21 and 24% above that of the control yield (15910 kg DM ha⁻¹) for the respective treatments. The pasture response to DFE-N compared very favourably with that of N fertilisers but DFE enhanced over a longer period. The authors attributed this response to a slow release of N from the organic N components in the DFE. The N uptake by the pasture was 14, 24, 19, 30 and 33% greater than that of the control (450 kg ha⁻¹) for each of the DFE treatments.

The winter period was unusually dry and low drainage volumes were recorded. Correspondingly, inorganic N leached from the highest DFE treatment (375 kg N ha⁻¹) was only 2.1 kg N ha⁻¹. Under a non-fertilised grazed treatment close by, 12 kg inorganic N ha⁻¹ were leached.

In summary, the DFE field studies show that for the same amount of total N applied, DFE will leach less inorganic N than inorganic fertilisers. On soils which are susceptible to bypass flow, significant amounts of untreated DFE can contribute to the drainage from the site due to the very dilute nature of DFE. In terms of pasture yield and N uptake, DFE appears to perform similarly to conventional inorganic fertiliser but the response of the pasture is over a longer period.

2.4 DFE soil process studies

Others researchers have investigated in more detail the actual turnover processes that occur when DFE is applied onto the soil. Di *et al.* (1999) labelled the inorganic fraction of DFE and NH₄Cl with ¹⁵N. While

this labelling technique enabled only 30% of the N in DFE to be tracked it did provide useful information on how this fraction of the DFE responded in the soil.

The predominant form of inorganic N measured in the drainage was $^{15}\text{NO}_3$ (> 95%). Labelled N contributed 22% of the annual N leaching in the DFE treatment and 54-65% in the NH_4Cl treatment. This result was attributed to lower inorganic N content and increased microbial biomass growth and hence immobilisation in the DFE treatment. This stimulation of the microbial activity by DFE appears to maintain the dynamic inorganic N pool at a size to meet pasture N demands without large leaching losses occurring.

In the first harvest of pasture following the application, approximately 45% of the pasture N was derived from the inorganic ^{15}N in the NH_4Cl but only 17% in the DFE treatment. On an annual basis, the percentage of herbage-N derived from the applied ^{15}N was lower in the DFE than that from the NH_4Cl (approximately 5% compared to 13%). The total quantities of herbage produced and N removed by the pasture in each of the treatments were similar, indicating that a significant proportion of the herbage-N in the DFE treatment must have been contributed from the organic N fraction and from stimulated mineralisation of soil N. The pasture in both treatments took up a similar percentage (approximately 24%) of the ^{15}N -labelled inorganic N that was applied.

Two studies investigated the dynamics of DFE applied onto soil by measuring gross N mineralisation, nitrification rates, microbial-C and -N, and extracellular enzyme activities under laboratory conditions at various water potentials (Zaman *et al.*, 1999b) and under field conditions (Zaman *et al.*, 1999a).

In the laboratory study, the addition of DFE at the equivalent rate of 200 kg N ha^{-1} significantly increased N mineralisation, $1.7\text{-}7.0 \mu\text{g N g}^{-1} \text{ soil day}^{-1}$ compared to the control at $1.2\text{-}3.8 \mu\text{g N g}^{-1} \text{ soil day}^{-1}$. The increase was greatest for the first measurement (Day 8) and had returned to background levels by Day 16. This effect was attributed to the presence of readily mineralisable organic substrates with low C:N ratios and stimulated soil microbial and enzymatic activities by the organic C and nutrients in the DFE. The nitrification rate which increased from 1.2 to $1.9 \mu\text{g N g}^{-1} \text{ soil day}^{-1}$ in the DFE treatment over the 90 days of the experiment, was greater than in the control, which remained relatively constant at $0.85 \mu\text{g N g}^{-1} \text{ soil day}^{-1}$. Soil microbial biomass-C was also significantly increased due to DFE application; during the first 30 days of incubation it was approximately 30% above that of the control. After this period it was no longer significantly elevated. The effect on soil microbial biomass-N was longer lasting than that on biomass-C with the difference being significant for 60 days. Enzyme activities were also significantly increased immediately after the addition of DFE and then declined with time. The optimum soil water potential for gross N mineralisation and nitrification rates, microbial and enzyme activities was -10 kPa as compared to 0 or -80 kPa . The total solids content of the DFE used in this study was extremely high at 8.7% compared to an average value for DFE of 0.90% for 63 sites reported by Longhurst *et al.* (2000).

The soil NH_4 concentration in the DFE treatment was higher than in the control for the first eight days and then decreased, with the NO_3 concentration increasing correspondingly. The correlation between gross N mineralisation, microbial-C and -N and enzyme activities in the DFE soil confirmed that the mineralisation of this material is a sequence of different microbial and extracellular enzyme activities.

To check whether the response found in the laboratory was valid under field conditions the same ^{15}N dilution technique was applied to field cores by Zaman *et al.* (1999a). The gross mineralisation rate in the DFE treatment increased to $6.1 \mu\text{g N g}^{-1} \text{ soil day}^{-1}$ during the first 16 days and then declined back to the control level of approximately $1.1 \mu\text{g N g}^{-1} \text{ soil day}^{-1}$. These rates are similar to that measured under the laboratory conditions. The nitrification rate increased from 1.0 to $1.5 \mu\text{g N g}^{-1} \text{ soil day}^{-1}$ by Day 16 and then declined to the control level of approximately $0.8 \mu\text{g N g}^{-1} \text{ soil day}^{-1}$. As in the laboratory incubation, the extracellular enzyme activity increased after the application of the DFE and then declined with time. Microbial biomass-C was enhanced by approximately 40% on Day 1 and Day 4 after the addition of DFE. It then decreased to 20% above the control value on Day 30 and then remained elevated but not significantly different compared to the control until the end of the experiment at Day 120. The biomass-N was also significantly influenced by the application of DFE with a similar 40% increase over the control at Day 1. After this date the biomass-N in the control increased until Day 16 while the DFE treatment remained relatively stable at the elevated level until Day 30 when it was 30% above the control level. Both the control and the DFE biomass-N then decreased in the remainder of the experiment to the same level at Day 120. The C:N ratio of the microbial biomass was very low (range 3-5) both in this study and the accompanying laboratory study, which makes the interpretation of these results difficult.

The rate of gross N mineralisation was best correlated to the microbial biomass-C and -N in this field study whereas in the laboratory study it was best related to the protease enzyme activity.

While these process studies present some evidence of enhanced microbial activity and higher gross N mineralisation rates following the addition of DFE to the soil, this response appears to last only for 30 days. This short period would appear to be in conflict with the relatively long response time that pasture exhibits for DFE applied under field conditions. From the few published process studies on DFE in soils, it can be concluded that the N dynamics are not yet sufficiently well understood to reliably predict the fate of the N in DFE.

There are also no studies available that have attempted to link quantitatively the C and N dynamics in DFE or the C mineralisation rates of the different fractions within DFE. Such studies are essential for the understanding and modelling of the fate of organic effluents applied onto soils in a process-based framework.

2.5 N simulation models

Many N simulation models of differing levels of sophistication with different objectives and intended uses have been developed. Models can be classified into two basic groups, deterministic and stochastic (Adiscott and Wagenet, 1985). Deterministic models presume that the system operates such that a given set of events leads to a uniquely definable outcome, whereas stochastic models presuppose the outcome to be uncertain and are developed to account for this uncertainty. The deterministic models can be further subdivided into mechanistic and functional models, though in reality the division is not always clear and there is more of a continuum than a division. Mechanistic models incorporate in detail all of the fundamental mechanisms of the process whereas the functional models incorporate simplified descriptions that require less input and computational description. Due to the level of detail, mechanistic models are

very rare and most of the published models are process-based models that are somewhere between the two extremes of mechanistic and functional. A process-based model includes simplified descriptions of the important processes of the system being modelled.

Some of the available N models have focused on a single process or a subset of processes within the N cycle; others have attempted a more complete description of the total N cycle as shown in Figure 2.1. It is beyond the scope of this literature review to present in detail the extensive number of N models available. The 1996 edition of the CAMASE register (Plentinger and Penning de Vries, 1996) describes 98 agroecosystem models which include soil processes and the Soil Organic Matter Network lists 27 soil organic matter models in operational use. Rather than detail these models, this review will firstly outline the common elements that exist within complete N simulation models. The method of describing the decomposition of organic materials and associated microbial dynamics in a range of simulation models will then be reviewed in more detail. For completeness, the reader is referred to the list of published reviews and comparisons of C and N models given in Table 2.3.

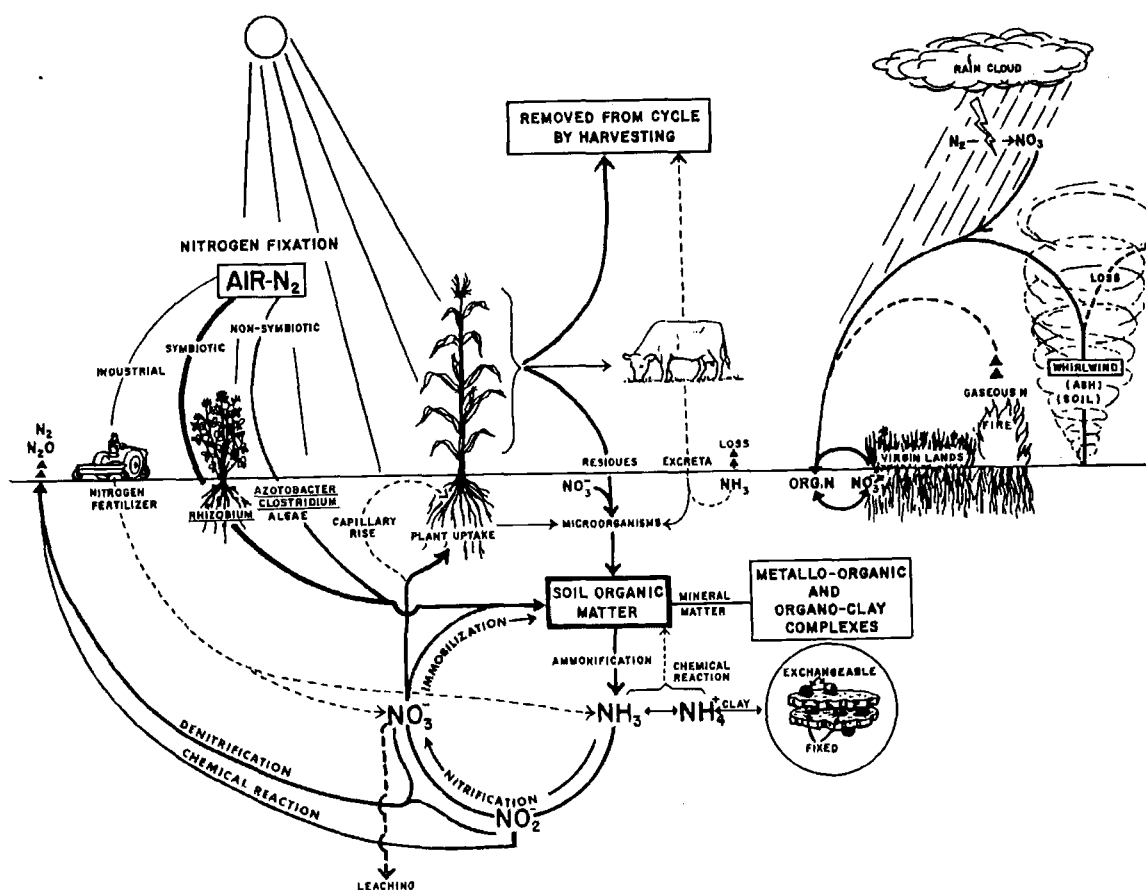


Figure 2.1 Complete nitrogen cycle (Stevenson, 1982).

Table 2.3 Published reviews of N and/or C models with comparisons of performances, in chronological order.

Title	Reference	Models considered (where named)
Simulation of nitrogen behaviour of soil-plant systems	Frissel and van Veen (1981a)	UCD-RANN, NFLUX, NITROSIM, WASTEN, NDS, M ₃ , TRAMIN, N1NIT, PHOENIX, PAPRAN, NLOSS, SL3, ANAER
Comparison of six simulation models for the nitrogen cycle in the soil	De Willigen and Neeteson (1984)	
Barley straw decomposition in the field: A comparison of models	Andren and Paustian (1987)	
Nitrogen turnover in the soil-crop system: Proceedings of a workshop	Groot <i>et al.</i> (1990)	LEACHM, SOILN, ANIMO, DAISY, SWATNIT, TRITSIM, WHNSIM
Modelling plant and soil systems	Hanks and Ritchie (1991)	SOYGRO, DRAINMOD, CERES-N, EPIC
Modelling of Geo-Biosphere Processes: Validation of Agroecosystems Models	McVoy <i>et al.</i> (1993)	SOIL, OPUS, AGROSIM, ECOSYS, WAVE, DAISY, CANDY, N-SIM,
Field validation and comparison of LEACHM and NCSWAP models for predicting nitrate leaching	Jabro <i>et al.</i> (1993)	LEACHM, NCSWAP
Analysis and field-evaluation of the CERES model's soil components: Nitrogen transfer and transformations	Gabrielle and Kengni (1996)	CERES, NCSOIL, SLM
Evaluation of 3 simulation models used to describe plant residue decomposition in soil	Jans-Hammermeister and McGill (1997)	PHOENIX, ECOSYS
Modeling carbon and nitrogen processes in soils	Molina and Smith (1998)	NCSOIL, VERBERNE, CENTURY, RothC-26.3, DAISY, SOMM, Q-SOIL, CANDY, SOMNET
A review of carbon and nitrogen processes in four soil nitrogen dynamics models	Wu and McGechan (1998)	SOILN, ANIMO, DAISY, SUNDIAL

Some models that describe the fate of organic materials do not include N, rather they describe the decomposition of the C component of the added organic material and resident soil organic matter. These models, while not including N, are still very relevant, as it is the decomposition of the C which is the driving force in the microbial availability of the organic N fraction.

To allow this review to focus on C and N decomposition methods, the detailed description of how environmental effects such as temperature, soil moisture, pH, clay content and soil CEC have been included in specific models has not been described. Generally, these environmental factors are included as a simple multiplying factor (0-1.0) in the relevant equations.

2.6 Framework of N models

Conceptually, three compartments are represented within a complete N cycle model; the atmosphere, the soil, and the plant. The transfer between these three compartments occurs through gaseous and water fluxes, with the water carrying nutrients.

The hydrological processes of rainfall, evaporation, transpiration and temperature are described in the atmosphere compartment. It is also the eventual sink for any gaseous products such as CO₂, nitrous oxide, and ammonia that may be state variables within the model, as well as a source for other gases such as oxygen, and N.

Many of the N transformations such as mineralisation, nitrification, immobilisation, denitrification, volatilisation and plant uptake (Figure 2.1) occur in the soil compartment. The plant is one of the main sinks for inorganic N as well as being a source of N through processes such as N₂ fixation by legumes, root death and turnover.

Many of the microbial degradation processes that occur in the soil under ideal conditions can be described by a first-order decay process (Hamaker and Thompson, 1972), where the organic material decreases at a rate proportional to its mass (M). This loss rate is expressed mathematically as:

$$\frac{dM}{dt} = -\mu M \quad (2.1)$$

where:

μ = first-order decay rate constant

M = mass of material.

This can be integrated and written as

$$M(t) = M_o \exp (-\mu t) \quad (2.2)$$

where:

$M(t)$ = mass of material at time t

M_o = initial mass of material at time zero.

Consequently, organic material undergoing first-order decay loses mass at a rate exponentially declining with time.

2.7 Model complexity

Forty soil N and/or C models that potentially could be used to describe the fate of DFE onto land have been reviewed, as listed in Table 2.4. The models have been classified on the basis of either being N, C or N and C models, and whether the soil microbial biomass is modelled explicitly. This classification results in:

1. **N only models** (9 models)
 Explicit microbial biomass pool (2 models)
2. **C only models** (5 models)
 Explicit microbial biomass pool (4 models)
3. **C and N models** (26 models)
 Explicit microbial biomass pool (17 models)

The number and description of the organic pools included in each model with an increasing level of complexity is given in Table 2.4.

Table 2.4 **Summary table of N and/or C models reviewed in increasing level of complexity.**

Name of model or author if unnamed	References	Number of explicit microbial biomass pool(s)	Number of organic matter pools (microbial biomass pools not included)	Names of organic matter pools (microbial biomass pools not included)
N only models				
Addiscott	Addiscott and Whitmore (1987)	None	One	Organic N
Lafolie	Lafolie (1991)	None	One	Organic matter
Cabon	Cabon (1991)	None	One	Organic N
Mehran	Mehran and Tanji (1974)	None	One	Organic N
Bhat	Bhat <i>et al.</i> (1980)	None	Three	Mineralisable waste, mineralisable soil organic N, stable soil organic N
WHNSIM	Huwe and van Der Ploeg (1991)	None (implicit)	Three	Most easily, easily, not easily mineralised organic matter
Reddy	Reddy and Khaleel (1979)	None	Three	Mineralisable N from waste, residual organic N, native soil organic matter
van Veen and Frissel (1 st Generation)	Frissel and van Veen (1981b)	One	Five	Straw, organic matter in wastewater, manure, old organic matter, dead microbial biomass
Jenkinson	Jenkinson and Parry (1989)	One	Two	Root, stubble and immobilised N, humus N

Name of model or author if unnamed	References	Number of explicit microbial biomass pool(s)	Number of organic matter pools (microbial biomass pools not included)	Names of organic matter pools (microbial biomass pools not included)
C only models				
Reddy	Reddy <i>et al.</i> (1980)	None	Three	Phase I, II, III decomposition
Jenkinson	Jenkinson and Rayner (1977) Parshotam (1995)	One	Four	Decomposable and resistant plant material, physically stabilised organic matter, chemically stabilised organic matter.
Jenkinson	Jenkinson <i>et al.</i> (1987)	Two	Four	Labile and stable plant material, humified organic matter, biologically inert organic matter
Sallih	Sallih and Pansu (1993)	One	Five	Decomposable and resistant plant material, labile soil organic matter, humified stable organic matter, chemically stabilised organic matter.
Darrah	Darrah (1997)	One	Three	Soluble C, insoluble plant-derived C, insoluble C from dead microbial biomass
C and N models				
NITROSIM	Rao <i>et al.</i> (1981)	None	Three	Available C, added organic matter, total soil C
SOMM	Chertov and Komarov (1997)	None	Three	Litter, humus with undecomposed organic debris, soil humus
NLEAP	Hansen <i>et al.</i> (1995)	None	Three	Residues, fast soil organic matter, slow soil organic matter
PAPRAN	Seligman and van Keulen (1981)	None (implicit)	Two	Fresh organic matter, stable organic matter
SOILN	Johnsson <i>et al.</i> (1987; Paustian <i>et al.</i> (1990)	None (implicit)	Three	Litter, faeces and manure, soil humus

Name of model or author if unnamed	References	Number of explicit microbial biomass pool(s)	Number of organic matter pools (microbial biomass pools not included)	Names of organic matter pools (microbial biomass pools not included)
C and N models				
SWATNIT	Vereecken <i>et al.</i> (1991)	None (implicit)	Three	Litter, faeces and animal manure, soil humus
LEACHM	Hutson and Wagenet (1992); Jabro <i>et al.</i> (1995)	None (implicit)	Three	Litter, faeces and animal manure, soil humus
SUNDIAL	Bradbury <i>et al.</i> (1993)	One	Three	Root, stubble and immobilised N, humus N
ANIMO	Rijtema and Kroes (1991)	None (implicit)	Four	Soluble C, added fresh organic matter, root exudates, soil organic C
CENTURY	Parton <i>et al.</i> (1987); Paustian <i>et al.</i> (1991)	None (implicit)	Five	Structural plant residue, metabolic plant residue, active soil C, slow soil C, passive soil C
NCSOIL	Molina <i>et al.</i> (1983)	Two	Four	Plant residues - liable, plant residues - resistant, humads - labile, humads -- resistant
NCSOIL (II)	Nicolardot <i>et al.</i> (1994)	Two	Three	Residues, humads, stable organic matter
van Der Linden	van Der Linden <i>et al.</i> (1987)	One	Six	Farmyard manure, green straw manure, roots, easily decomposable, recalcitrant, old organic matter,
TRAMIN	Juma and Paul (1981)	One	Seven	Metabolite-C and -N, C only, active SOM, stabilised SOM, old organic matter, decomposable fresh, slowly decomposable
DAISY	Hansen <i>et al.</i> (1991); Jensen <i>et al.</i> (1994)	Two	Five	Dead native soil organic matter (SOM ₀ , SOM ₁ , SOM ₂) added organic matter (AOM ₁ , AOM ₂)

Name of model or author if unnamed	References	Number of explicit microbial biomass pool(s)	Number of organic matter pools (microbial biomass pools not included)	Names of organic matter pools (microbial biomass pools not included)
C and N models				
N1NIT	Bosatta (1981)	One	Two	Organic C and N (proteins), C only (cellulose)
Whitmore	Whitmore <i>et al.</i> (1991)	One	Four	Decomposable and resistant plant material, humified organic matter, inert organic matter
Blagodatsky	Blagodatsky and Richter (1998); Blagodatsky <i>et al.</i> (1998)	One	Two	Soluble C, insoluble soil organic matter
Thornley	Thornley and Verberne (1989)	One	Four	Faeces, dead shoot, dead root, dead soil organic matter
Verberne	Verberne <i>et al.</i> (1990)	Two	Six	Decomposable, structural, resistant, protected and non-protected active soil organic matter, stabilised organic matter
van Veen and Frissel (2 nd Generation)	Frissel and van Veen (1981b)	One	Five	Proteins, sugars, cellulose, lignin, resistant microbial biomass residues
van Veen and Frissel (3 rd Generation)	van Veen <i>et al.</i> (1984); van Veen <i>et al.</i> (1985)	One	Seven	Rapidly, slowly decomposable, recalcitrant, decomposable microbial material, recalcitrant (non-protected) plant material, active (protected) organic matter, old organic matter
van Veen and Frissel (4 th Generation)	van Veen <i>et al.</i> (1984); van Veen <i>et al.</i> (1985)	Two	Six	Rapidly decomposable, slowly decomposable, unprotected recalcitrant plant and metabolite pool, active (protected) OM, old OM and decomposable metabolites.

Name of model or author if unnamed	References	Number of explicit microbial biomass pool(s)	Number of organic matter pools (microbial biomass pools not included)	Names of organic matter pools (microbial biomass pools not included)				
C and N models								
RZWQM	USDA-ARS-GPSR (1992)	Three	Five	Structural residue, metabolic residue, fast organic matter, intermediate and slow organic matter.				
PHOENIX	McGill <i>et al.</i> (1981a); McGill <i>et al.</i> (1981b)	Two	Eight	Live root and shoot, standing dead structural and metabolic, litter structural, litter metabolic, humads, resistant soil organic matter				
ECOSYSTEM	Grant <i>et al.</i> (1993)	Twelve (Three biomass pools for each of the four organic substrates)	Twenty	Level One Organic substrates	x	Level Two - plant residue	Level Three protein Carbohydrate Cellulose Lignin - animal manure - active soil OM - passive soil OM	C and N x sorbed stabilised
				Four soluble organic pools for each Level Two pool Eight microbial residues for each biomass pool except storage				

2.8 N only models

The simplest form of N model has one pool of organic N. The transfer from the organic pool to the ammonium pool is via a one-way flow, modelled using zero-order (Addiscott and Whitmore, 1987) or first-order kinetics (Lafolie, 1991).

An improvement on this simple model is to recognise that the N flow can be in both directions and that inorganic N can also be immobilised into organic N. The immobilisation flows have been modelled using first-order kinetics (Cabon, 1991; Mehran and Tanji, 1974).

The next level of model complexity describes the organic N more accurately by a number of pools that are chosen to reflect the microbial availability of various organic fractions that may be present.

The model developed by Bhat *et al.* (1980) for the simulation of the fate of N in farm wastes applied onto land effectively uses two organic N pools:

- mineralisable waste
- mineralisable soil organic matter.

A third pool of stable organic matter is also included but no N was considered to be mineralised from this pool. First-order kinetics are used to simulate the flow of N from both mineralisable pools into the ammonium pool. The immobilisation of N is controlled by the C:N ratio of the waste material being added. If the C:N ratio of the added material is less than 20, it is considered to be mineralisable, with 80% of the added material going into the mineralisable soil organic matter pool and the remainder to the stable soil organic matter pool. If the C:N ratio is greater than 20, immobilisation from the inorganic N pools occurs until the C:N ratio of the added material is down to 20.

The WHNSIM model (Huwe and van Der Ploeg, 1991) divides soil organic matter into three pools:

- most easily mineralised organic matter
- easily mineralised organic matter
- not easily mineralised organic matter.

Each pool has its own corresponding first-order rate constant to describe conversion from the organic to inorganic N fraction. Immobilisation from the inorganic fraction into the easily mineralised organic pool, where the microbial biomass is considered to be included, is simulated by zero-order kinetics.

In a model developed by Reddy and Khaleel (1979) for estimating the total potentially available N from soil receiving animal wastes the added organic waste N is described by two pools:

- mineralisable N
- residual organic N.

The soil organic matter is contained in one pool called:

- total soil organic matter.

The size of the mineralisable N pool in the waste is based on a C:N ratio of 23 being the equilibrium ratio between immobilisation and mineralisation. The amount of N greater than this critical N is considered to be the mineralisable N pool. The residual organic N is added into the total soil organic N which decomposes at a slower rate than that of the mineralisable N. The amount of potentially mineralisable N from the soil organic N pool is predicted from the relationship developed by Stanford and Smith (1972). This soil mineralisable N is combined with the mineralisable N from the organic amendment and the conversion to nitrate is simulated by first-order kinetics.

A microbial biomass-N pool is included in two N models which describe organic N decomposition. In the first model, by van Veen and Frissel (1st Generation) (Frissel and van Veen, 1981b) the immobilisation of inorganic N into the microbial biomass pool is controlled by the difference between the C:N ratio of the added material and the critical C:N for mineralisation/immobilisation, which in this instance was considered to be 20. The immobilisation/mineralisation process is described by first-order kinetics.

Added organic material is sub-divided into three pools:

- straw
- manure
- organic material in waste water.

The soil organic matter pools are described by:

- microbial biomass
- dead microbial biomass
- old organic matter.

All mineralisation rates are described by first-order kinetics. Two modifying terms are used to determine the actual rates of decomposition used. One term is a priming factor that accounts for the growth of the microbial pool. The other is an availability factor that is dependent on the type of organic material and the fraction of organic material that has already been decomposed. This availability factor requires the time or the extent of decomposition that each added organic material has undergone to be tracked. This requirement of tracking of each organic addition is a significant disadvantage in this approach.

The second model (Jenkinson and Parry, 1989) that uses a microbial biomass-N pool is very similar in structure to the C model proposed by the same authors (Jenkinson *et al.*, 1987), which is discussed later. The added plant residue and root stubble is combined with the immobilised N to form a single input pool of N that is split between humus N and microbial biomass-N pools. The decomposition of organic material in the humus and microbial biomass pools is controlled by first-order kinetics. The product of decomposition is split between inorganic N, microbial biomass-N and humus N pools. The humus and microbial biomass pools subsequently undergo further first-order decomposition, which again is split between microbial biomass, humus and inorganic N pools. The inorganic N is available to be either taken up by the plant or lost from the system.

In summary, N only models describe the fate of the organic N in DFE applied onto soil in a functional manner. However, as they do not explicitly model C that controls the N transformation processes, they can

not be considered to be realistic descriptions of the processes occurring. Due to their lack of process descriptions, functional models can not be expected to accurately simulate conditions that are different to those under which the model has been developed. As the goal was to develop a process based C and N model useful over a wide range of conditions, the approaches advocated in these N only models did not meet our requirements.

2.9 C only models

Obviously, models which only describe C transformations are not developed with the objective of predicting the fate of organic N. Nevertheless, the way in which the C processes are described in these models is relevant as C turnover is the driving force in the transformation of organic N.

A conceptual decomposition sub-model proposed by Reddy *et al.* (1980) suggests that the decomposition of organic material from animal wastes, plant residues and native soil organic matter can be described by dividing the organic material into a number of decomposition steps. These steps were referred to as:

- phase I
- phase II
- phase III

of the decomposition process as a whole. Each stage has its own first-order decomposition rate and an amount of C that this rate applies to. The decomposition process as a whole is described by applying the relevant first-order kinetics to the appropriate pool size that depends on the stage of decomposition of the original organic material.

A more complete model of the C cycle was developed by Jenkinson and Rayner (1977) to describe data from the Rothamsted experiments. This model separates the added plant residue into two compartments:

- decomposable plant material
- resistant plant material.

The soil organic matter is divided into three organic matter pools:

- soil microbial biomass
- physically stabilised organic matter
- chemically stabilised organic matter.

C mineralisation from each of the five pools is modelled using first-order kinetics to describe the rate at which C is lost, and set proportions of the decomposed material are allocated to the microbial biomass, physically and chemically stabilised organic matter pools and microbial respiration. A simplification was made so that the same proportions were allocated to each of the receiving pools irrespective of which organic matter pool was being decomposed. The model operates on a monthly time step.

This model was modified further by Jenkinson and Parry (1989) with the splitting of the microbial biomass pool between a zymogenous microbial biomass, which receives C decomposed from the added organic material, and an autochthonous microbial biomass pool, which uses C from the humified organic

matter (physically stabilised). The chemically stabilised pool is called the biologically inert organic matter pool and is not considered to be active in the C dynamics. The model incorporates the effect of soil texture by altering the partition between CO₂ evolution and the other receiving pools on the basis of soil classes. Bradbury *et al.* (1993) further extended this approach into a C and N model called SUNDIAL.

The Jenkinson and Rayner (1977) model was also used as a basis for a model proposed by Sallih and Pansu (1993). The soil organic matter had an additional labile soil organic matter pool added and as Jenkinson and Parry (1989) proposed, the chemically stabilised organic matter pool was not considered to be an active pool.

In a model developed to describe the rhizosphere environment (Darrah, 1997), the population dynamics of the soil microbial biomass were modelled in more explicit detail than just a C balancing approach, with one pool representing the microbial biomass. In this model, only soluble C is considered to be a substrate for microbial growth. Three C pools decompose into this soluble C fraction. The first is the soluble C from root exudates which directly contributes into this pool. The other two pools, insoluble C from the roots and dead microbial biomass, must undergo a decomposition process before they can contribute to the soluble substrate pool. The rate of decomposition from these two insoluble pools is assumed to follow Michaelis-Menten kinetics relating the amount of insoluble C, the size of the microbial biomass pool and the maximum rate of decomposition. The Michaelis-Menten kinetics limit the maximum rate of a reaction, unlike first-order kinetics which is not limited.

The growth dynamics of the microbial biomass is determined using the specific growth rate approach. This is based on the maximum specific growth rate de-rated for the actual soluble C concentration in the soil using a Michaelis-Menten equation. The maintenance energy requirement is subtracted to determine the actual specific growth rate for the microbial biomass.

The three C decomposition models described above have been further developed by various workers through the addition of N components, as discussed in Section 2.1.

2.10 C and N models

There are numerous methods to describe the interactions between the dynamics of C and N cycles and thereby provide a better process-based representation.

The incorporation of a microbial biomass component into a model is a key criterion in determining the degree of sophistication of a model. The simplest implementation of a microbial biomass component is to treat the microbial biomass simply as a receiving pool for all or part of the decomposing C substrate. The microbial biomass can either be implemented as a separate pool or as part of a larger pool. If an explicit microbial biomass pool is implemented, the size of this pool may be used in simulating the degradation process of the C substrates. A more sophisticated approach is to incorporate a maintenance energy requirement for the microbial biomass. Generally this is done by using an efficiency factor to split the pool of decomposed C between that lost as CO₂ in meeting the maintenance energy requirement and that C which is actually assimilated into microbial-C. Some models use a humification factor to separate the C that is not respired into microbial biomass and a more resistant pool to simulate humification, as shown in

Figure 2.2. Depending on the level of complexity of the model, the efficiency factor used can be varied, according to the type of microbial biomass undertaking the degradation and the substrate being degraded. The most complex models explicitly describe microbial growth and decay. In these models various techniques can be coupled to describe the interaction between the predicted microbial growth and the decomposition of substrate.

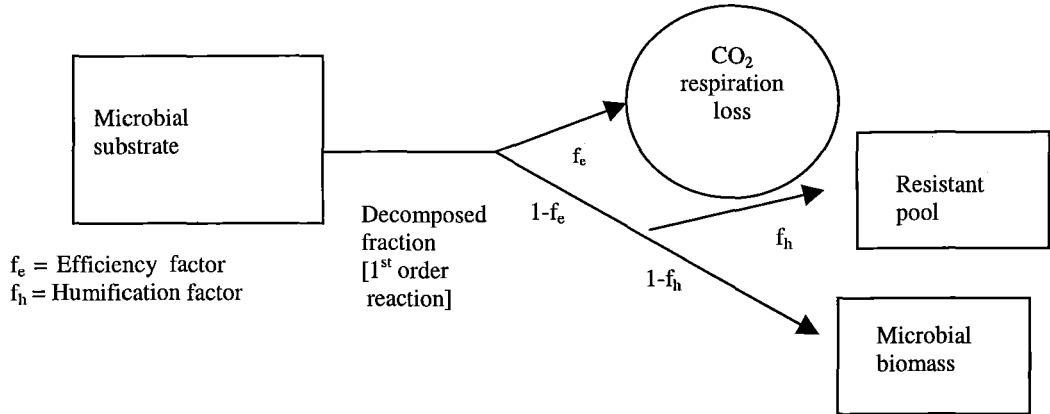


Figure 2.2 Typical organic decomposition model with microbial growth and accompanying humification algorithm.

The interaction between C and N in the microbial growth process has been described by Parnas (1974). In this model the organic material R is considered to be made up of proteins and RNA type materials, which have both C and N, and other compounds such as cellulose and starch which contain C, but no N. The microbial biomass that grows on R, provided other nutrients are in excess, does so at a growth rate G which is considered to be a function of the available C and N concentrations. C is required as an energy source and for growth while the N is only required for the latter purpose.

Therefore, there exists a certain critical ratio between C and N for growth which is defined as:

$$x/f_n \quad (2.3)$$

where:

$$x = f_c/F \quad (2.4)$$

x = total C used by the organism for a unit increase in microbial biomass

f_n = average fraction of N in the decomposer's cell

f_c = average fraction of C in the decomposer's cell

F = ratio of C assimilated to C decomposed.

This description implies that C is the growth-limiting factor when the C:N ratio of the substrate is less than x/f_n and N is limiting when the C:N ratio is greater than x/f_n . The change in the amount of C in the substrate can be written as

$$\frac{dC}{dt} = -xGB \quad (2.5)$$

where:

G = growth rate for the decomposers

B = microbial biomass of the decomposers per unit of soil.

Assuming that the release of N is proportional to C, the change in N can be written as:

$$\frac{dN}{dt} = \frac{dC}{dt} C : N \quad (2.6)$$

and

$$\frac{dN}{dt} = -(f_n GB - i) - m \quad (2.7)$$

where:

i = rate of immobilisation

m = rate of mineralisation of N.

When compounds containing both C and N (CN) and compounds containing only C (C only) are present the question arises as to whether the CN compounds are decomposed for the C or the N. The strategy proposed by Parnas (1974) was that when the system is in a N limiting state, the CN pools act as a N source and the C only material is the C source. When C is limiting the microbial development, the CN pools become primarily a C source.

The growth rate for the decomposers, (G), is a function of both the C and the N which can be described by a double Michaelis-Menten expression (Equation 2.8):

$$G = G_{max} \frac{CN}{(k_c + C)(k_n + N)} \quad (2.8)$$

where:

G_{max} = maximal growth rate for given environmental conditions for use of substrate R when N and C are non-limiting

N = organic N and NH_4

k_c = Michaelis-Menten constant which describes the C concentration when G equals $G_{max}/2$

k_n = the same as k_c except for N.

The following sections of this review discuss the methods used to describe the decomposition of organic materials and associated microbial dynamics in various simulation models. The discussion is structured to present the models with an increasing level of complexity as given in Table 2.3. The emphasis in this discussion is to highlight differences in the various approaches employed as the level of complexity increases in the models. To avoid unnecessary repetition, the decomposition method in a model is the same as used in the previous model and only the differences are discussed unless otherwise explicitly stated.

2.11 NITROSIM

NITROSIM (Rao *et al.*, 1981) represents the simplest category of combined C and N models. This model combines two models previously discussed, the N only and C only models of Reddy and Khaleel (1979) and Reddy *et al.* (1980). In this combined model no microbial biomass pool is simulated. The C modelling is only used to quantify the amount of available C needed to determine the potential denitrification. The C:N ratio of the added material determines the size of the mineralisable N pool.

2.12 SOMM

The SOMM foodweb model developed by Chertov and Komarov (1997) was primarily developed to describe the decomposition of leaf litter in forests. It considers that the decomposition rate of a specific pool is linked to a type of fauna capable of decomposing or involved in the humification process of that substrate. The ash and N content of the pool also effect the decomposition rate. The three pools simulated in the model are:

- litter
- humus combined with undecomposed organic debris
- soil humus.

Separate first-order kinetic equations are applied to describe the C or N mineralised and that humified. When more than one type of soil fauna are considered to undertake the humification process, multiple first-order equations are applied to the pool.

2.13 NLEAP

The NLEAP (Nitrate Leaching and Economic Analysis Package) model was developed as a screening tool for identifying land management practices that can result in nitrate leaching (Hansen *et al.*, 1995). The model contains pools of:

- residues
- fast soil organic matter
- slow soil organic matter.

The control between net N mineralisation and immobilisation from the residue pool depends on the current C:N ratio of the residue pool and a threshold C:N ratio of 30. The first-order rate coefficient used for simulating the decomposition from the residue pool is dependent on the material being decomposed and the current C:N ratio. In general, fresh materials have a higher decomposition rate until a C:N ratio is reached where most of the easily decomposable material has been broken down and a lower rate is appropriate. Once a C:N ratio of 8-15 is reached, depending on the residue, the remaining C and N in the residue pool are transferred into the fast soil organic matter pool. The C lost as CO₂ is determined from an efficiency factor applied to the decomposed material, as described in Figure 2.2. As no biomass pool exists, the remaining C that has been decomposed is considered to be humified to the next slowest decomposing pool in a cascading manner.

2.14 PAPRAN

PAPRAN (Seligman and van Keulen, 1981) was developed as a single season simulation model where organic N is considered to exist in only two pools:

- fresh organic matter
- stable organic matter.

The microbial biomass is considered to be part of the fresh organic matter pool. The decomposition of the fresh organic matter is simulated using variable first-order rate constants. If the C:N ratio of the combined fresh organic pool and inorganic N is above 25, the decomposition rate is reduced as insufficient N is available for microbial growth.

When the C:N ratio is above 25, immobilisation by internal recycling into the fresh organic matter pool occurs and CO₂ is lost by respiration. The amount of N that is considered to be immobilised and recycled back into the microbial biomass is calculated using a biosynthesis efficiency factor of 0.4 and a C:N requirement of 8 for microbial biomass. When the C:N ratio drops below 25, net mineralisation occurs and a small fraction is transferred to stable organic matter. The stable organic matter has a constant C:N ratio and mineralises C at a much slower first-order rate than the fresh pool.

2.15 SOILN

The SOILN model (Bergstrom *et al.*, 1991; Wu *et al.*, 1998) which was developed by Johnsson *et al.* (1987; 1991) uses two pools for added organic material:

- litter
- manure

and a third pool for the soil C:

- slowly cycling soil humus.

The decomposed C is divided into three pathways: CO₂, stabilised organic matter that contributes to the humus pool, and the microbial biomass/metabolites material that is returned into the litter pool, as shown in Figure 2.2. The C:N ratio of the recycled product transferred into microbial biomass and that of humified are assumed to be equal.

Mineralisation or immobilisation of N is determined by assuming that the C:N ratio of the microbial biomass and humification products are constant and equal and that the N made available in the decomposition process is determined by the C:N ratio of the litter pool. If insufficient inorganic N is available to meet the C:N balancing requirement, decomposition will be postponed until sufficient inorganic N is available. Conversely, if excess N is produced from the decomposition process N is mineralised into the NH₄ pool. The humus pool also mineralises N at a first-order rate into the inorganic N pool. The SWATNIT (Vereecken *et al.*, 1991) and LEACHM models (Hutson and Wagenet, 1992) use the same concepts and equations as described by Johnsson *et al.* (1987).

2.16 ANIMO

In the ANIMO model (Rijtema and Kroes, 1991) the C sources are differentiated between those in solution and those contained in a solid phase. The C description is also based on the approach of Jenkinson and Rayner (1977). Four organic pools are used:

- soluble C
- added fresh organic matter
- root exudates
- soil organic C (includes microbial biomass).

The soil organic C pool is split into a number of fractions, each specified by a C:N ratio and an associated first-order decomposition rate. The added fresh organic matter must decompose into the soluble C pool before it is considered to be microbially available. The C in the two other pools, soil organic C and root exudates, can be used directly by the microbes. The mineralisation or immobilisation flows of N are calculated from the C:N ratios of the source and destination pools and the amount of C respired. As the biomass is considered to be contained within the soil organic matter pool, respiration and N mineralisation fluxes are calculated directly from this pool using first-order kinetics.

2.17 CENTURY

The CENTURY model (Parton *et al.*, 1987) contains three soil organic matter pools:

- active SOM
- slow SOM
- passive SOM

and two plant residue pools:

- structural plant material
- metabolic plant residue.

The active SOM pool is considered to consist of live microbes and microbial by-products as well as soil organic matter with a short turnover time (1-5 years). The slow SOM pool is material which is either physically protected or chemically more resistant to decomposition, with a turnover of 20-40 years. The passive SOM is the slowest available material and has a turnover of 200-1500 years. The added plant residue material is split between the faster metabolic and slower structural pools. The split between these pools is determined from the residues lignin:N ratio. The structural C first-order decomposition rate is controlled by the lignin content of the pool and the decomposed fraction is incorporated into the slow SOM pool. The non-lignin fraction of the structural plant material decomposes into the active soil C pool, with CO₂ losses determined from the efficiency factor which relates to soil type. The surface layers are considered to have lower decomposition rates due to soil moisture content effects. The fraction of the decomposition product going into a receiving pool is a function of soil type.

The N fluxes are determined from the C fluxes and the stoichiometry of the fixed C:N ratios of the receiving pools. The C:N ratio of the structural plant residue and the three SOM pools are fixed. The C:N ratio of the metabolic plant residue pool will vary depending on the C:N ratio of the incoming plant material.

2.18 NCSOIL

In NCSOIL (Molina *et al.*, 1983) there are three types of material which are considered available for microbial degradation:

- plant residues
- microbial biomass (Pool I)
- humads (Pool II).

Each of these pools is further subdivided into labile and resistant fractions. The residue plant material is considered to decompose into the microbial biomass pool and CO₂. The biomass pool decomposes into the humad pool and also recycles part of the decomposition product back into the microbial biomass pool to simulate succession, with a fraction being lost as CO₂. The microbial biomass pool is also a recipient for part of the decomposition product from the humad pool. The first-order decomposition coefficient and split of the decomposed material between labile and resistant pools are considered to be a function of the size of the microbial biomass pool.

2.19 NCSOIL II

The original NCSOIL model as described in Section 2.18 represented only the active fraction of the SOM and had been validated for field experiments up to 3-months in duration but was not considered suitable to simulate the gradual transfer of C and N into more stable organic fractions. The model was modified by Nicolardot *et al.* (1994) and called NCSOIL II for use with longer-term data. This modification was implemented by considering that the only organic pool that had both a labile and resistant fraction was the microbial biomass pool and a stable organic matter pool was added. This stable organic matter pool receives decomposition products from the humad pool. The NH₄ pool is the exclusive source of N immobilised into the microbial biomass pool.

2.20 van Der Linden

van Der Linden *et al.* (1987) developed a model based on the work of van Veen and Frissel (1981) to study the implication of long-term manure and crop-residue applications to different soils.

The four pools of organic soil material are:

- Pool 1 = easily decomposable, i.e. sugars, proteins and carbohydrates
- Pool 2 = recalcitrant and lignin-like fractions, which are slowly decomposable
- Pool 3 = old organic matter, which is only very slowly available
- Pool 4 = microbial biomass.

The three litter or residue pools are:

- farmyard manure
- straw and green manure
- roots.

These three litter inputs are split between Pools 1 and 2 depending on their composition. Part of the decomposition product from Pool 2 is transferred into Pool 3, the old organic matter pool, to simulate humification. The metabolites from microbial biomass death are split between Pools 1 and 2.

2.21 TRAMIN

Juma and Paul (1981) developed TRAMIN for use with tracer studies to simulate the mineralisation and immobilisation of soil N. Five soil organic matter pools and a soil microbial biomass pool are used:

- metabolites (C and N)
- C only pool
- active SOM
- stabilised SOM
- old organic matter
- soil microbial biomass.

The added plant residue material is split between:

- decomposable fresh material
- slowly decomposable material
- metabolite pool (if appropriate).

The decomposition of the substrates is described by first-order rates, and is independent of the size of the microbial pool. The rate of increase in microbial biomass-C and loss to CO₂ is controlled by the efficiency factor for each of the substrates. The amount of N that is immobilised is determined by the increase in microbial-C and the C:N ratio of the microbial biomass. Dead microbial biomass transferred into the active fraction of the SOM and metabolites is described by first-order kinetics. The receiving pools for the metabolites have fixed C:N ratios, and as microbial biomass dies the C and N are allocated into appropriate pools. As the metabolite-C pool has no N component, it can be used to receive any residual C. Humification without microbial mediation is considered to occur between the soil organic pools at a first-order rate.

2.22 DAISY

The DAISY model (Hansen *et al.*, 1991; Jensen *et al.*, 1994; Jensen *et al.*, 1997; Mueller *et al.*, 1998; Svendsen *et al.*, 1995) has organic matter divided into three main pools:

- dead native soil organic matter (SOM)
- microbial biomass (BOM)
- added organic matter (AOM).

Each of these main pools is further subdivided into two or three sub-pools, each one being characterised by a particular C:N ratio and a decay rate to describe the microbial availability of the substrate. The dead native soil organic matter has three sub-pools:

- SOM_0
- SOM_1
- SOM_2 .

SOM_0 is considered to be almost inert organic matter, and SOM_1 is considered to consist of chemically stabilised organic matter. SOM_2 is physically stabilised due to adsorption onto soil colloids or entrapment within soil aggregates.

Added organic matter AOM is split into:

- AOM_1
- AOM_2 .

AOM_1 consist of mainly cell walls, and AOM_2 is the water extractable fraction of the added material. Lignin or other resistant material is added into the SOM_2 pool.

The soil microbial biomass is subdivided into two pools, BOM_1 and BOM_2 , to describe the relatively stable and more dynamic parts of microbial biomass. The simulation of microbial biomass dynamics is based on growth efficiencies, maintenance respiration and rate coefficients. The AOM_1 pool is a substrate for both microbial biomass populations, while AOM_2 , which is the more easily available material, is considered as a substrate for only the more dynamic part of the microbial biomass. The C decomposed using first-order kinetics from the substrate pool is partitioned between microbial biomass and CO_2 using pool specific efficiency values. Each microbial biomass pool has a specific first-order death rate that is related to environmental conditions. The effect of soil type is incorporated into the decomposition values of the SOM_1 and SOM_2 and the death rate of BOM_1 . The C maintenance energy requirements are considered to be different for the two biomass populations.

2.23 N1NIT

The N1NIT model was developed by Bosatta (1981) for forest systems with organic residue split between three pools, two C only pools and one N only pool. The C is split between C originating from materials with a narrow C:N ratio such as proteins and those from a relatively wide C:N ratio such as cellulose. The organic N is in the N only pool.

The approach implemented follows closely that of Parnas (1974) as discussed in Section 2.9, where the decomposition population dynamics is simulated using a specific growth rate for the microbial biomass population. The immobilisation of C and N is based on these growth requirements and the C and N content of the microbial biomass. The microbial biomass-N requirement can be met from both inorganic N and organic N sources, taking into account an availability factor for the organic N.

The decomposition rate of the C substrate is determined from the growth of microbial biomass and an efficiency factor that relates microbial biomass production to C decomposed. The C respired as CO₂ is the difference between the C decomposed and that used for microbial growth.

Microbial biomass dies off at a first-order rate and contributes C to both organic N and C pools, pro-rated between them on the basis of the C:N ratio of the microbial biomass.

2.24 Whitmore

The initial model built by Jenkinson *et al.* (1987) for C dynamics was further developed to describe both N and C by Whitmore and Parry (1987).

The N dynamics are simulated by assuming that C:N ratios of all the pools except the easily decomposable pool are fixed. The easily and resistant decomposable plant material (C:N = 100) decompose to the same products: zymogenous microbial biomass (C:N = 15) and humified organic material. This process requires an input of mineral N. The ratio of microbial biomass formed to humus created is considered to be the same for all soils. The C lost as CO₂ in this decomposition was set as a fixed ratio of the products formed. The humus decomposes to mineral N, autochthonous microbial biomass, and humus, with fixed ratio losses of CO₂. Both microbial biomass pools break down in the same pathway as the easily decomposable plant material. Based on experimental evidence the proportions of decomposing N material that become mineral N or organic N are related to the clay content of the soil. This effect is modelled using the cation exchange capacity of the soil as a measure of the clay stabilisation effect. The ratio of CO₂ to the amounts of microbial biomass and humus produced are considered to be specific for each soil type.

A simpler version of this model, using only one soil organic matter pool, was developed by Whitmore *et al.* (1991).

2.25 Blagodatsky

The model developed by Blagodatsky and Richter (1998) attempts to describe the dynamics of microbial growth and N turnover under laboratory conditions in more detail by considering activity levels of the microbial biomass. Three organic matter pools are used in this model:

- soluble C
- microbial biomass
- insoluble soil organic matter.

C for microbial growth can only be consumed from the soluble C pool. The microbial biomass is considered to be either in an active or a dormant state, modelled using an index of the physiological state of the microbial biomass. This physiological index attempts to describe the environmental factors that control the microbial biomass transition from the dormant to the active state. The effect of the physiological state of the microbial biomass is incorporated into the microbial dynamics by multiplying the microbial biomass growth and death functions by this physiological index. It can be manipulated to either slowly return or rapidly return to dormant state after a period of excitation.

The growth of the microbial biomass is described by a Michaelis-Menten approach relating the maximum specific growth rate of biomass to the soluble C substrate. The net growth rate is determined by subtracting the dying biomass fraction and a biosynthesis efficiency value to account for reutilisation of the dead biomass. The actual microbial biomass death rate is related to the concentration of the soluble substrate available.

The consumption of the soluble substrate is the sum of the C taken up by the biomass for growth divided by a yield efficiency value which allows for respiration losses.

The model has three sources of CO₂:

- the maintenance component of the microbial biomass due to the utilisation of the soluble substrate
- the maintenance component due to the decomposition of the insoluble pool
- the maintenance component due to the recycling of the dead biomass.

The rate of decomposition of the insoluble C pool into soluble C and CO₂ is modelled using Michaelis-Menten kinetics depending on the amount of active microbial biomass and amount of insoluble C.

2.26 Thornley

As part of a larger model on integrated grassland grazing, a sub-model of N and C processes was developed by Thornley and Verberne (1989). There are three input pools:

- faeces
- dead shoot material
- dead root material.

Organic matter in the soil is described as:

- dead soil organic matter
- microbial biomass.

The faeces are split between a C only and an organic N pool with a fixed C:N ratio. This organic N pool is degraded using first-order kinetics to the soil ammonium pool and the associated amount of C is lost to CO₂. The faeces C only pool undergoes first-order decomposition and is humified into the dead soil organic matter pool. The decomposition of dead shoot-C and -N is also simulated using first-order kinetics, with all of the N being transferred into the soil organic matter pool. An accompanying C respiration loss is calculated on the basis of the amount of N transferred. The dead root-C and -N is treated in a similar manner but no C loss to respiration is simulated.

The only C pool used as a substrate for microbial growth is the dead soil organic matter pool. The associated microbial N requirement for growth is met from the available mineral N pool. The growth rate of the microbes is determined from the maximum growth rate, and from a double Michaelis-Menten expression for C and N substrate concentrations with a factor included to limit the size of the microbial population. This growth rate only applies to a fraction of the microbial biomass. This active fraction depends on factors such as population density, surface area factors and substrate distribution. The microbial biomass has a constant C:N ratio. The total amount of C that is decomposed from the dead soil organic matter pool is determined from the calculated biomass growth rate and the microbial efficiency value.

The microbial biomass dies at a specific death rate that can cause the population to asymptotically fall to a minimum. The C from the dead microbial biomass is all respired and the N is transferred into the available soil N pool in the form of ammonium. This available N pool is considered to be spatially separate from the uniformly distributed soil ammonium and nitrate pools and is formed from microbial activity and death. The microbial population preferentially uses this available N source for growth. The transfer from the available N pool to the soil ammonium-N pool is done via a “mineralisation pathway” by a spatial transfer process through diffusion. The immobilisation pathway, when N demands for growth can not be met from the available N pool, is also simulated by diffusion from both the soil nitrate and ammonium pools.

2.27 Verberne

In the model proposed by Verberne *et al.* (1990) the added residues are considered to consist of three fractions each with its own first-order decomposition constant. The pools are:

- decomposable material (DPM) - carbohydrates and proteins
- structural material (SPM) - cellulose and hemi-cellulose
- resistant material (RPM) - lignified structural material

Each of the pools is considered to have a fixed C:N ratio. The more available pools of decomposable and structural materials are microbially decomposed, while the lignin fraction is directly added into the active

soil organic matter pool. The soil organic matter is divided using the scheme as proposed by van Veen *et al.* (1984):

- microbial biomass
- protected active soil organic matter
- non-protected active soil organic matter
- stabilised soil organic matter.

The concept of physically protected soil organic matter with a lower microbial availability and a non-protected pool with a higher availability for the same material is included in the model. The microbial biomass is also divided into protected and non-protected components. The protected fraction is equivalent to that microbial population present in soil not recently disturbed by tillage or large additions of fresh organic matter. The protected soil organic matter and microbial biomass have much lower decomposition rates than the corresponding non-protected pools.

The decomposition rate of the structural and resistant plant residue follows Parton *et al.* (1987) utilising the size of the lignin pool. The resistant residue material is added equally to the protected and non-protected soil organic matter pool. Decomposing microbial biomass is distributed between these two pools as a function of soil type.

2.28 RZWQM

In RZWQM (USDA-ARS, 1992) the organic matter and N (OMNI) cycling sub-model was based on the concepts of the NTRM (Clanton *et al.*, 1983), PHOENIX (McGill *et al.*, 1981b), CENTURY (Parton *et al.*, 1987) and Frissel and van Veen (1981b) models. The organic matter is distributed over five computational pools and is decomposed by three microbial biomass populations.

The crop residue consists of:

- slow pool (structural)
- fast pool (metabolic)

with soil organic matter described by:

- fast organic matter pool
- intermediate organic matter pool
- slow organic matter pool.

The fast organic matter pool equates to the potentially mineralisable N pool in soil without amendments or crop residues. The microbial biomass is divided into three populations: two heterotrophic populations, (soil fungi and facultative anaerobic bacteria) and one autotrophic (nitrifier) population.

The first-order decomposition rate is a function of temperature, size of microbial biomass population, pH, soil salinity and oxygen concentration. Initially a fraction of the decay product is transferred into inter-pool transfer; the remaining C is then split between respiration and microbial biomass assimilation using an efficiency factor. The net assimilation or mineralisation of the N associated with the C decay depends

on the C:N ratios of the degraded and receiving pools. Sufficient inorganic N must be present for net immobilisation to occur, otherwise microbial growth and organic matter decay cannot proceed.

The autotrophs (nitrifiers) are a special case as their energy source is NH_4 and the C from CO_2 . The growth rate of the microbial biomass of nitrifiers is related to the rate of the nitrification process using an efficiency factor. This factor partitions the nitrified NH_4 between microbial biomass and NO_3 .

The denitrifiers are a special case of microbial biomass, which under O_2 limiting conditions will use NO_3 as an alternative electron donor. When NO_3 is depleted and C substrate is still available, CH_4 production is simulated. The denitrification process is modelled using first-order kinetics based on nitrate concentration. The rate constant is a function of temperature, salinity, biomass population, C substrate concentration and pH. When NO_3 is present under anaerobic conditions the amount of C decay is determined from the denitrification rate using a conversion factor. This C is taken up by the facultative anaerobic microbial biomass and distributed between respiration as CO_2 and/or CH_4 and assimilated as microbial biomass-C. The rate at which each of the organic matter pools contributes is based on pro-rating the decay rate from each of the contributing organic matter pools compared to the total decay rate from all of the pools.

The death of microbial biomass from each of the microbial biomass pools is calculated using first-order kinetics based on the size of the microbial biomass pool. The first-order death rate is a function of temperature, oxygen conditions, pH and C substrate. Minimum microbial biomass levels are set for each of the three populations.

2.29 van Veen and Frissel (2nd Generation)

In the second-generation model developed by Frissel and van Veen (1981b) the organic amendments are split into pools of similar materials:

- proteins
- sugars
- cellulose
- lignin

with microbial pools of:

- microbial biomass
- resistant microbial biomass residue.

The growth of the microbial biomass is controlled by the availability of both C and N. The decomposition of C is considered to be the result of microbial biomass growth; consequently if no growth occurs then no decomposition occurs. All organic N is in the protein pool, except for that in the microbial biomass pools. Microbial biomass is considered to be able to utilise dead microbial biomass as a substrate.

The growth of microbial biomass is assumed to occur according to Michaelis-Menten kinetics, with the maximum growth rate specific to the type of substrate. The size of the microbial biomass pool capable of utilising the substrate is also a factor in determining the amount of microbial growth that can occur. This

fraction capable of utilising a particular substrate pool is determined from the ratio of the amount of C in that pool to the total amount of C present. The growth rate of the microbial biomass also considers the availability of inorganic N.

The N mineralisation rate is determined from the decomposition rate of the protein pool by dividing the C transfer rate by the C:N ratio of the protein pool. Immobilisation requirements are determined from the microbial biomass growth divided by the C:N ratio of the microbial biomass. The growth of microbial biomass using the dead microbial biomass pool is calculated from first-order kinetics.

2.30 van Veen and Frissel (3rd Generation)

The soil organic matter and the microbial debris received more attention in the third generation model by the same authors (Frissel and van Veen, 1981b; van Veen and Frissel, 1981). Five pools of organic matter are considered as substrate for microbial biomass. The pools that describe the organic matter are:

- well decomposable fresh material (sugars and carbohydrates), Pool 1
- slowly decomposable fresh material (cellulose), Pool 2
- easily decomposable N substances (proteins and amino sugars), Pool 3
- readily decomposable (well decomposable active material), Pool 4
- resistant active material, Pool 5
- inert organic material, Pool 6.

The difference between Pools 4 and 5 is that Pool 5 consists of organic material that is adsorbed onto clay or entrapped in soil aggregates but is chemically identical to Pool 4. Pool 6 is resistant to microbial decay. As the C in a combined CN pool is used, the corresponding amount of N is transferred into the mineral N pool. The N flux from Pool 6 is the only flux not mediated by microbial biomass.

The death rate of the microbial biomass is related to the substrate from which the microbial biomass developed. Those that grow from more easily available compounds die at a faster rate than those grown from less available substrates. The model does not track five different microbial biomass pools; rather it assumes that the size of a particular microbial biomass population is proportional to the quantity of substrate present. The products from the death of the microbial biomass are split between Pool 4 (well decomposable active material) and Pool 5 (resistant active material).

The release of N, growth of microbial biomass and CO₂ production from the resistant organic matter are all based on first-order kinetics. The humification from Pool 5 to Pool 6 without microbial mediation is also simulated by first-order dynamics.

2.31 van Veen and Frissel (4th Generation)

The third generation model was further developed by van Veen *et al.* (1984) and van Veen *et al.* (1985). In this version the description of plant and soil organic matter, the variation of the C:N ratio of the microbial biomass, effects of drying and re-wetting the soil and the microbial biomass turnover were either newly included or modified.

The scheme proposed is based on work by Juma and Paul (1981) where plant material is considered as consisting of three fractions:

- rapidly decomposable
- slowly decomposable
- unprotected recalcitrant plant and microbial pool.

The soil organic matter is split between:

- active (protected) organic matter
- old organic matter
- decomposable microbial material.

Laboratory experiments with labelled substrates showed that soils with a higher clay content generally keep higher proportions of C and N as microbial biomass. Clay content may either affect the biosynthesis efficiency values and/or death rates of microbial biomass. This observed result led to changes in the description of microbial death. Like the organic matter, the microbial biomass is split between a protected and unprotected fraction dependent on soil type. The death rate of the protected fraction is lower than that of the unprotected fraction. Most of the C and N that is released from dead microbial biomass enters the decomposable and recalcitrant soil fractions and only a small amount, dependent on soil type, enters the active organic matter pool.

The C:N ratio of the microbial biomass can vary depending on the soil mineral N concentrations. Accumulation of extracellular organic matters during soil drying can also occur.

The enhanced microbial activity and greater N mineralisation following the re-wetting of dry soils has been simulated by moisture effect factors on the microbial death rate. The death of microbial biomass is modelled using first-order kinetics and the wetter the soil the lower the rate of death. The re-wetting effect is simulated by assuming that the day following a wetting-up event the soil is at optimal soil moisture irrespective of the actual moisture content. After 24 hours the moisture effect reverts to the actual moisture content effect.

2.32 PHOENIX

A model developed by McGill *et al.* (1981a, 1981b) describes the transformation and transport processes of C and N in native grassland. In total, twelve pools of organic matter are used in the model. Two pools describe microbial biomass:

- bacteria combined with actinomycetes
- fungi.

Two pools describe soil organic matter:

- humads
- resistant soil organic matter.

Four pools describe plant component:

- live roots
- live shoots
- standing dead metabolic
- standing dead structural.

Two pools describe litter component:

- litter plants
- litter microbes.

The litter is further divided, with each of the dead plants and dead microbes pools having a metabolic and structural component. The structural component has a C:N ratio of 150 for plants and 30 for the microbial fraction. The metabolic component that consists of membranes, organelles and cytoplasm is assumed to have a C:N ratio of 5 for plants and 3 for the microbial fraction.

The decomposition and uptake processes are modelled separately for each of the two microbial biomass pools but have the same generalised form. The structural component of litter is decomposed at a constant rate modified by the C:N ratio, size of the microbial biomass population, as well as density effects of substrate and microbial biomass. The assimilation of this decomposition product into the microbial biomass and into the humad component is proportional to the humification factor.

The humad decomposition uses a Michaelis-Menten expression based on the solution concentration of humad, and the size of the microbial biomass population. A humification factor is used to split the decomposed C between microbial assimilation and the resistant soil organic matter.

The decomposition of the resistant soil organic matter is at a first-order rate, incorporating the size of the microbial biomass pool. All decomposition products from this pool are considered to be microbially assimilated.

The decomposition of the metabolic litter component uses a Michaelis-Menten expression based on the dissolved metabolic-C concentration and the size of the microbial biomass population. The microbes assimilate all the C and N made available by the decomposition of this metabolic component of litter.

The microbial respiration is modelled for both soil microbial groups using the same approach, but different parameter values. The C released as CO₂ is the sum of the C that is required for maintenance for the existing microbial biomass population plus the fraction of the C which is taken up but not used for microbial growth. The microbial death rate is modelled as a function of lethal stresses such as drying, freezing and a density dependent rate.

2.33 ECOSYSTEM

The ECOSYSTEM model (Grant and Rochette, 1994; Grant *et al.*, 1993) is the most complex model of the C and N soil-plant system. There are four levels used to describe each C and N compound.

At the highest level four pools are implemented:

- organic substrates (S)
- soluble organic pools (P)
- microbial populations (M)
- microbial residues (Z).

Each pool type then has three levels to describe biological organisation:

i = highest level: substrate/microbe complex

j = middle level: structural or kinetic compound

k = lowest level: elements such as C or N within each component.

The organic substrate (S_i) in each soil layer is represented by four substrate/microbe complexes:

i = x is animal manure

= y is plant residue

= m is active soil organic matter

= n is passive soil organic matter.

Each of the substrates (S_i) is resolved into kinetic components (S_{ij}). A kinetic component is assumed to be a homogeneous substrate of differing resistance to microbial decomposition. For example the plant residue substrate S_{yj} is resolved into:

j = d is protein

= e is carbohydrate

= f is cellulose

= g is lignin.

The active soil organic matter S_{mj} has two components:

j = s is sorbed

= t is stabilised.

The C pool in each of the organic substrates described above (S_{ijk}) is described by:

k = C,

and the N pool by:

k = N.

Each of the S_i components (animal manure, plant residue, active and passive soil organic matter) is also associated with a microbial population M_i . Each of these microbial populations has structural components of the microbial biomass described by M_{ij} :

j = l is labile

= r is resistant

= w is storage.

These microbial structural components are used to calculate kinetic components for the microbial biomass which may be either active (a) or quiescent (q). The products from microbial death of M_{ijk} become microbial residues with the same subscripting, but labelled as Z_{ijk} .

The microbial decomposition (Ds_{ijc}) of the C fraction for each component of substrates (S_{ijc}) is determined from:

- the size of the total active microbial biomass associated with that decomposition of that particular substrate, (M_{iac})
- the associated decomposition rate of the specific material, (Ds_{ijc})
- the fraction of the total C present in all of the substrates that this particular component represents, i.e.

$$Ds_{ijc} = Ds'_{ijc} \sum_{i=1}^I M_{iac} \{ S_{ijc} / \sum_{j=1}^J S_{ijc} \} \quad (2.9)$$

The microbial residues (Z_{ijk}) are decomposed in the same manner. The factors of accessibility and microbial density in the decomposition process have been included by using substrate concentration and microbial biomass population terms in calculation of the Ds' term.

The decomposition of the N component (i.e. S_{ijn} and Z_{ijn}) are related to the C decomposition by the relevant C:N ratio.

The decomposition products from all of the substrates and metabolites are considered to be part of a soluble organic pool that is associated with each of the substrate-microbe complexes. This material is considered to be adsorbed and desorbed onto soils using Freundlich isotherm kinetics which include the effect of the total soil C. A fraction of the adsorbed material (S_{msik}) is irreversibly fixed (V_{msik}) into the stabilised component of S_m . Once stabilised, the soluble C represents accumulated products that are no longer available for desorption.

The dissolved C remaining in solution is the material that is considered to be a substrate for microbial growth. The specific growth respiration rate per unit of active microbial biomass is calculated using a Michaelis-Menten expression based on the dissolved C substrate and the potential growth respiration rate under non-limiting conditions. This specific rate is converted to the aerobic growth respiration rate by multiplying it by the amount of active biomass and the actual oxygen available in the soil.

The potential uptake of soluble C by the active soil microorganism under a non-limiting nutrient supply is determined from this aerobic growth respiration and the growth efficiency factor (taken as 0.6). The net uptake by the microbial biomass is the difference between this potential uptake and the aerobic growth respiration. The actual uptake of C by the microbial biomass may be in fact limited by microbial-N, so the C:N ratio of the microbial biomass is used in a Michaelis-Menten type expression to determine the actual C uptake rate. C that is taken up by the microbial biomass is either stored, or becomes labile or resistant microbial biomass. The stored fraction is transferred into the labile and resistant pools using a first-order relationship and split between the two receiving pools. The uptake of organic N from the dissolved soluble components is coupled to that of the organic C by the C:N ratio of the dissolved soluble components. The N is split only between labile and resistant microbial biomass with no contribution to the storage component.

Each of the microbial biomass populations requires maintenance energy that is associated with the maintenance respiration ($R_{m_{ijc}}$) component. This respiration requirement is determined from the specific maintenance energy requirement and the size of the microbial biomass. The total C evolved as CO_2 is the sum of this maintenance respiration component and the C that is respired as CO_2 in the growth process.

Mineralisation/immobilisation of N is controlled by the C:N ratio of the microbial biomass population. By comparing the existing C:N ratio to that of the maximum ratio that the microbial biomass can maintain, a rate constant for the mineralisation or immobilisation of N is determined. The maximum C:N ratios for each of the labile and resistant microbial biomass pools are different. Soluble NH_4 is considered to be the preferred source of N for immobilisation with NO_3 being used if sufficient NH_4 is not available.

The active microbial biomass is considered to be all of the labile microbial biomass pool plus a fraction of the resistant microbial biomass. The remainder of the resistant microbial biomass (I_{rk}), not associated with the labile fraction, is considered to be quiescent (M_{ijk}).

Each microbial biomass is considered to undergo first-order inactivation or death from the active to the quiescent process, using a first-order rate approach. A fraction of this loss of active microbial biomass is transferred to the organic substrate through the passive substrate-microbe complex (S_{njc}) using the humification pathway, with the remainder going to microbial residues (Z_{ijk}).

2.34 Conclusions

While many models exist for describing the fate of organic matters in the soil, the irrigation of DFE onto land has some unique characteristics that require special consideration in selecting a model that can accurately represent the processes.

The first characteristic recognises that DFE is a mixture of both dissolved and particulate organic matters with a range of microbial availabilities. While most of the more complex models do allow for differing microbial availabilities in the added residue pools, only three models (ANIMO, DAISY and PHOENIX) have a residue pool that is soluble. Two other models (Blagodatsky and ECOSYSTEM) do include a soluble organic pool which is implemented as a receiving pool for decomposed C from other contributing pools. In all five models the C in the dissolved pool is considered to be immediately available for microbial consumption. PHOENIX does have the capability to simulate two different C pools that have a soluble C fraction, and these pools have different adsorption and microbial uptake characteristics. No existing model offers the flexibility of a range of microbial availabilities in a dissolved organic residue pool.

DFE also has a particulate C fraction that has been measured in the leachates from DFE-irrigated soils. Any candidate model thus must have the ability to describe the filtration and transport of particulate organic matters. Additionally, this particulate fraction needs to have a range of microbial availabilities. None of the models reviewed had the capability to transport particulate C down the soil profile with an irrigation or water flux event.

It has been found that preferential flow can dominate the quality of the leachate from irrigated DFE under certain soil and management conditions. It is considered essential that any model capable of simulating the fate of irrigated DFE needs to have the capacity of simulating bypass flow. Only one model reviewed, RZWQM, had a two-domain flow model (immobile/mobile) to provide this capability.

The three key microorganism groups responsible for specific functions in the soil are heterotrophs, nitrifiers and facultative anaerobes (denitrifiers). To accurately represent the processes these three microbial biomass pools are responsible for, it is necessary to simulate individual biomass pools. Only one model (RZWQM) could offer this level of process description. However, approximately a quarter of the models did allow for different biomass pools, based on their substrate or their environmental resilience (protected/non-protected).

Four of the models reviewed incorporated the concept of a change in the activity level of the microbial biomass which is dependent on substrate supply as well as environmental conditions. A physiological activation index, which controlled the transition of the microbial biomass from a dormant to an active state, was used by Blagodatsky. ECOSYSTEM used the concept of quiescent microbial biomass pools to control microbial activity, while PHOENIX and Darrah used different maintenance and growth rates for the microbial populations. After the addition of organic matter to the soil, the change in activity level of microbial biomass is considered essential to accurately simulate the microbial dynamics.

In summary, no single model of the 40 models reviewed was capable of modelling the processes involved in the application of DFE onto the land in the required detail. While several models have useful algorithms for describing some of the processes involved, no model could provide the detailed descriptions of the movement and transformations that occur when a two-phase dilute organic effluent such as DFE is irrigated onto the soil, as well as describing the microbial transformation processes. This thesis describes the development and testing of a simulation model to address these needs.

2.35 References

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Chapter Three

Immobilisation and mineralisation of C and N from DFE during laboratory soil incubations

The objectives of this Chapter are to:

Assess the likely environmental effects of current permitted annual loading rates of DFE

Gain a practical understanding of the key processes involved when DFE is added to soil

Concomitantly investigate C and N mineralisation and microbial biomass dynamics

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3.1 Introduction

Dairy farm effluent (DFE) is a mixture of dairy cow faeces, urine, and wash-down water, formed during the cleaning of the milking parlour and associated holding yards. DFE is a very dilute organic effluent, comprising a soluble fraction and an organic solids fraction ($> 0.2 \mu\text{m}$); the solids content is generally $< 1\%$ (Barkle *et al.*, 1994; Longhurst *et al.*, 2000). Typically, 60-85% of the total N present in the effluent is in an organic form (Barkle *et al.*, 1995; Selvarajah, 1996). Most of this organic N comes from the faeces, which consist of the organic solids fraction, such as undigested dietary constituents, undigested microbial cells and their residues, plus cells and enzyme residues from the animal's digestive system. The soluble fraction includes any soluble material from faeces plus urine. The urine contributes some organic compounds, but 60-90% of the total N in urine is urea, which is rapidly hydrolysed to ammonium (Whitehead, 1995). The interaction of these inorganic and organic, and soluble and solid fractions during the decomposition of the complex mixture DFE is insufficiently understood. Separation of DFE into a dissolved and a particulate fraction is likely to occur when DFE is irrigated onto land.

To minimise the risk of contamination of surface waters, regulatory authorities in New Zealand advocate irrigation onto land as the preferred treatment method for DFE. In the Waikato, one of the major dairying regions of New Zealand, the proportion of farmers who irrigate DFE onto pasture has risen from 35% to nearly 70% between 1993 and 1997 (Selvarajah, 1998). Little information is available to assess the effects that currently permitted annual loading rates ($150\text{-}200 \text{ kg N ha}^{-1}$; EW 1994, ARC 1999) have on the receiving environment (Selvarajah, 1996). These loading rates are not necessarily matched to the ability of the soil-plant system to assimilate the N, resulting in the risk of environmental contamination by nitrate leaching.

To establish justifiable loading rates, information about the short- and long-term turnover of DFE and associated microbial dynamics is needed. Such information is scarce, as existing data from North America and Europe (e.g. Cumby *et al.*, 1999) are not directly applicable to New Zealand conditions, due to DFE in New Zealand having a lower total solids and nutrient content and being irrigated daily onto pasture without previous storage.

We investigated the effect of two loading rates ("standard DFE", "high DFE") on the microbial turnover of DFE, assuming that the mineralisation of DFE would be better understood by concomitantly investigating net C and N mineralisation and microbial biomass dynamics. We also investigated the microbial availability of the soluble fraction of the complex substrate DFE ("soluble DFE"). To achieve this, we compared the effect of a high loading of soluble DFE on microbial growth and respiration to that of a defined soluble source of C and N ("glucose plus ammonium").

3.2 Material and methods

3.2.1 Soils and effluent

Soil from the 0-10 cm depth layer of the A-horizon of a Te Kowhai silt loam was collected under pasture from Number 1 Dairy, Dairying Research Corporation, Ruakura Research Centre in Hamilton, New Zealand. The Te Kowhai soil is a Typic Orthic Gley (Hewitt, 1992, New Zealand Classification) or a Typic Ochraqualf (Soil Survey Staff, 1990, USA Classification) representative of large areas of land onto which DFE is irrigated (Singleton, 1991). The particle size distribution in the sampled depth was 36% clay, 55% silt, and 9% sand (Singleton, 1991). Total soil C was 3.54% and N was 0.34% (C:N = 10.4). The field-moist soil was sieved through a 5-mm sieve, mixed, and air-dried to approximately 30% gravimetric moisture content. The standard DFE loading rate was based on the recommended hydraulic loading rate for a single DFE application (EW, 1994), while the high DFE loading was an extreme case, where double the permitted annual N loading rate was applied in one application (Table 3.1).

Table 3.1 C and N loadings (mg kg⁻¹ soil), pH and hydraulic loading (HL, mm), with resulting N and C loading on areal basis (kg ha⁻¹). TOC total organic C, DOC dissolved organic C, TKN total Kjeldahl N.

Treatment	TOC	DOC	TKN	NH ₄ -N	pH	HL	N loading	C loading
	(mg kg ⁻¹ soil)					(mm)	(kg ha ⁻¹)	(kg ha ⁻¹)
Standard DFE	410	136	60	19	8.2	20	68	465
High DFE	2322	688	303	52	8.2	30	345	2632
Soluble DFE	990	990	529	410	9.2	20	601	1122
Glucose + NH ₄ -N	5000	5000	500	500	5.4	20	568	5667

The soluble DFE loading resulted from the highest possible concentration of dissolved C that was obtainable by filtration of faeces diluted with urine in a ratio similar to that found in DFE. A high glucose and ammonium loading was chosen for the defined substrate treatment to ensure substantial microbial growth occurred. As the DFE collected from Number 1 Dairy was very dilute, additional faeces and urine were added to increase the N concentration to a more representative level (standard DFE: TKN 302 mg N l⁻¹, TOC 2049 mg C l⁻¹) (Longhurst *et al.*, 2000). The high treatment had additional faeces and urine added to make the C and N concentrations representative of an extreme loading (high DFE: TKN 1011 mg N l⁻¹, TOC 7740 mg C l⁻¹). The soluble DFE fraction (“soluble DFE”) was obtained by filtering a faeces and urine mixture through a 0.1 µm hollow fibre cartridge (Amicon Hollow Fibre Cartridge, Model H1MP01-43). For the defined C and N treatment, powdered glucose and ammonium sulphate were mixed into the soil and deionised water was added to make the water content similar to that of the standard DFE treatment.

3.2.2 Experimental

N and C loading rates of the four treatments are summarised on a mass (mg kg^{-1} soil) and an approximate areal basis (kg ha^{-1}) in Table 3.1. All amendments were applied to 1290 g of soil at 29% gravimetric water content. At this water content, the effluent treatments could be applied to the soils to bring them to approximately 60% of their water-holding capacity.

The standard and high DFE treatments were mixed with spatulas to ensure the effluents were evenly distributed. The amendments increased the water contents in the standard DFE, soluble DFE and glucose treatments to an average of 58% WHC. To achieve the required N-loading in the high DFE treatment the hydraulic loading had to be increased to 30 mm, resulting in 70% WHC. The soils were maintained at 25°C in low-density polyethylene bags that allow for gaseous transfer but maintain soil water contents relatively stable in the medium-term. Inorganic N, soluble C and C_{mic} were determined on 3 replicate 20 g samples on Days 0, 2, 9, 16, 23, 44, 113, and Day 244.

Microbial respiration was measured on separate batches of soil (10 g equivalent dry weight, 3 replicates) kept in sealed 1.1 vessels at 25°C for 50 days with 1 ml headspace samples taken for CO_2 determinations. The containers were vented to the atmosphere when CO_2 levels in the vessels approached 1%. Carbon dioxide evolution from the treatments was measured hourly for the first 48 h and then regularly but less intensively until Day 50 when the CO_2 respiration rates of three of the four treatments were not greater than the unamended control.

3.2.3 Analyses

All effluent analyses were done in triplicate. Kjeldahl N measurements were made using microdigestion (Bergersen, 1980) followed by microdistillation (Jackson, 1962) and titration. $\text{NH}_4\text{-N}$ was measured using standard autoanalyser techniques (Blakemore *et al.*, 1987). Total C in the effluents was measured using the acid dichromate method based on that of Tinsley III (Kalembasa and Jenkinson, 1973). Dissolved C components of the standard and high DFE were obtained by filtration through 0.2 μm cellulose acetate filters and measured using an automated C analyser (Shimadzu, TOC5000), which uses combustion followed by non-dispersive infrared detection of CO_2 gas. All C measurements made with the acid dichromate method were multiplied by 1.19 to enable direct comparison to the measurements made by the C analyser (Wu *et al.*, 1990). C_{mic} was estimated by the chloroform-fumigation-extraction method (CFEM) (Vance *et al.*, 1987) with C in 0.5 M K_2SO_4 measured by the automated C analyser. The k_{EC} value used was 0.42, resulting from adjusting the value of Sparling *et al.* (1990) of 0.35 for the TOC method used (Wu *et al.*, 1990). CO_2 respired in headspace gas was measured by an IRGA CO_2 analyser. The soil nitrate and ammonium concentrations were measured on the unfumigated K_2SO_4 extracts (1:4 soil:extractant ratio) using standard auto-analyser techniques (Blakemore *et al.*, 1987).

3.3 Calculation of net C and N mineralisation

Net C mineralisation (Figure 3.1b) was calculated as the difference in CO₂ evolution of the amended treatments and the control (Figure 3.1a), as in all studies using unlabelled substrate, assuming that there was no priming effect. Preliminary experiments with soluble DFE and soil sterilised by autoclaving had shown that 71% of the abiotic evolution of CO₂ occurred in the first hour after DFE was added to the soil, and that the evolution was completed after 4 h. We assumed this effect was due to CO₂ displacement from solution caused by the decreased pH when the alkaline DFE (Table 3.1) was added to the soil at pH 5.4 (Sparling and West, 1988). All respiration reported here has been corrected for this abiotic component, which amounted to maximal 3% of the applied C in the standard and high DFE treatments and to 24% in the soluble DFE treatment. The net effect of substrate amendment on inorganic N concentrations (Figures 3.4 and 3.5) was calculated by subtracting the concentrations measured in the control from the concentrations measured in the amended treatments. Net mineralisation of organic DFE-N (NNM) was calculated by additionally subtracting the amount of amended inorganic N in the DFE treatments.

3.3.1 Statistics

All results are expressed on an oven-dry basis (105°C, 24 h) and, unless otherwise stated, presented as means of 3 replicates \pm standard error. For the sake of clarity, standard errors of the net C mineralisation (Figure 3.1b) are only shown after the end of the most intensive measurement period (Days 0-10). Differences in CO₂ evolution, C_{mic}, and inorganic N between treatments were tested using one-way ANOVA and subsequent least significant difference (l.s.d.) tests at $P \leq 0.05$ using the SYSTAT 9 statistical software (SPSS Inc., Chicago, 1996).

3.4 Results

After Day 113, water contents in all treatments dropped strongly. As the decreasing water contents will have affected the turnover processes, the data from Day 244 have been excluded from the analysis.

3.4.1 C mineralisation

During the whole measurement period, CO₂ evolution of the standard DFE treatment was only slightly, but still significantly, higher than that of the control, whereas all other treatments lay well above (Figure 3.1a). At Day 50, the cumulative CO₂ evolution of the standard DFE treatment was not any more significantly higher than that of the control. Standard deviations are not shown in Figure 3.1a, as they were generally smaller than the size of the symbols (all CV < 7%). Expressing the CO₂ data as percentage of the C applied underlines that the extent and the kinetics of the cumulative net C mineralisation differed between the four treatments (Figure 3.1b). Overall net C mineralisation was highest for glucose (60.7 \pm 0.8%) and soluble DFE (58.1 \pm 1.9%), intermediate for high DFE (48.4 \pm 0.5%) and lowest for standard DFE (29.7 \pm 2.4%). Net C mineralisation of glucose, soluble DFE and standard DFE was finished at

Day 13, whereas the mineralisation in the high DFE treatment continued until the end of the measurements at Day 50 (Figure 3.1b). The standard and high DFE treatments both had near-linear initial responses to substrate amendment, while the soluble DFE and the glucose treatments were characterised by a lag-phase followed by a large CO₂-flush (Figure 3.2).

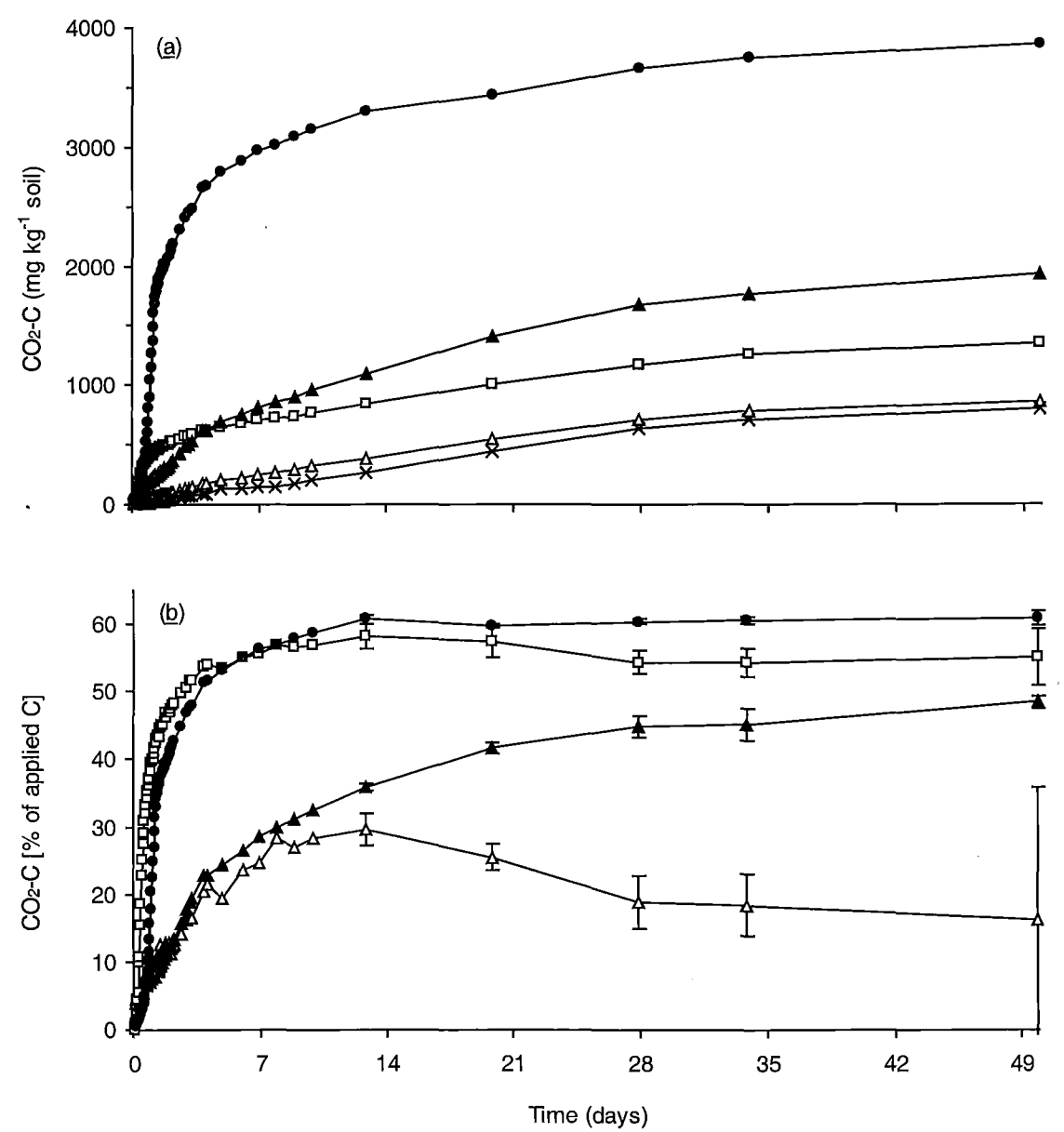


Figure 3.1 (a) Cumulative CO₂-C evolution (mg kg⁻¹ soil) over the measurement period of 50 days. Mean of n = 3; all coefficients of variation < 7%. (b) Cumulative CO₂-C as % of applied C (Control subtracted). Mean of n = 3 ± standard error (for measurements after Day 10). x Control, Δ Standard DFE, ▲ High DFE, □ Soluble DFE, ● Glucose + NH₄-N.

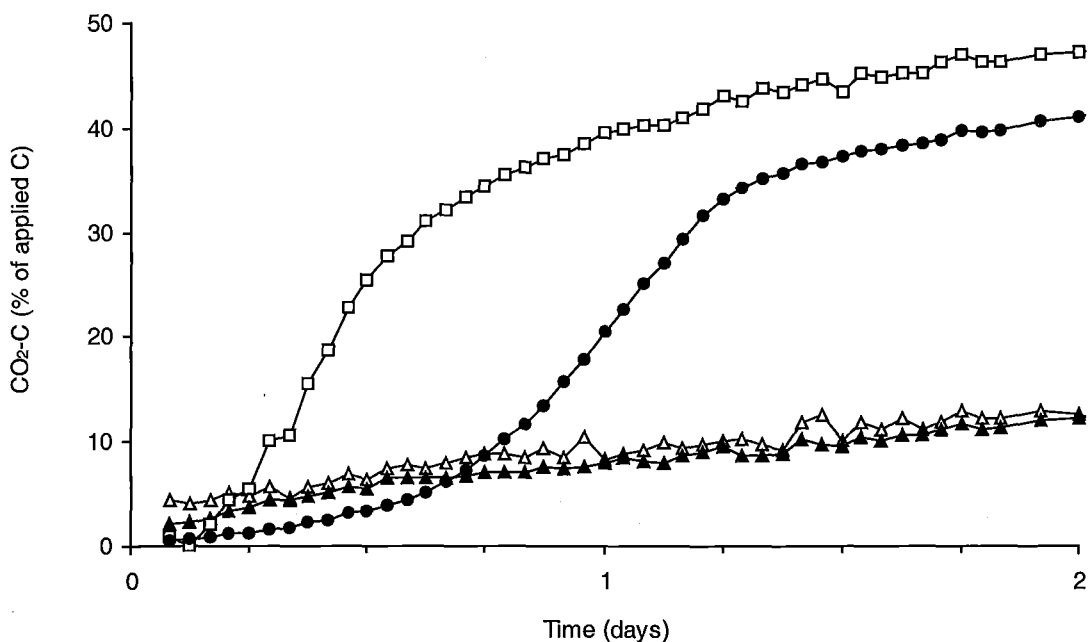


Figure 3.2 Cumulative CO₂-C evolution of the first 2 days (Enlargement of Figure 3.1(b)).
 △ Standard DFE, ▲ High DFE, □ Soluble DFE, ● Glucose + NH₄-N.

3.4.2 C immobilisation

The C_{mic} concentration of the control treatment (Day 0: $1034 \pm 96 \text{ mg kg}^{-1}$) increased slightly during the first 2 days after water amendment and then gradually decreased to $72 \pm 7\%$ of the initial value at Day 113 (Figure 3.3). DFE amendment at the standard rate had only a minor effect on C_{mic} , with a significantly lower concentration than the control at Day 9 and a higher one at Day 23. The high DFE treatment tended to support a higher C_{mic} concentration than the control, with the differences statistically significant at Days 23 and 113. The soluble treatment did not increase C_{mic} and had significantly lower microbial-C than the control from Day 9 through to Day 113. In the glucose treatment, C_{mic} could not be calculated at Day 2 because more C was extracted in the unfumigated than in the fumigated sample (negative C flush). C_{mic} was significantly enhanced at Days 9 and 23, but had dropped back to the level of the control by Day 44 and was below the control at Day 113.

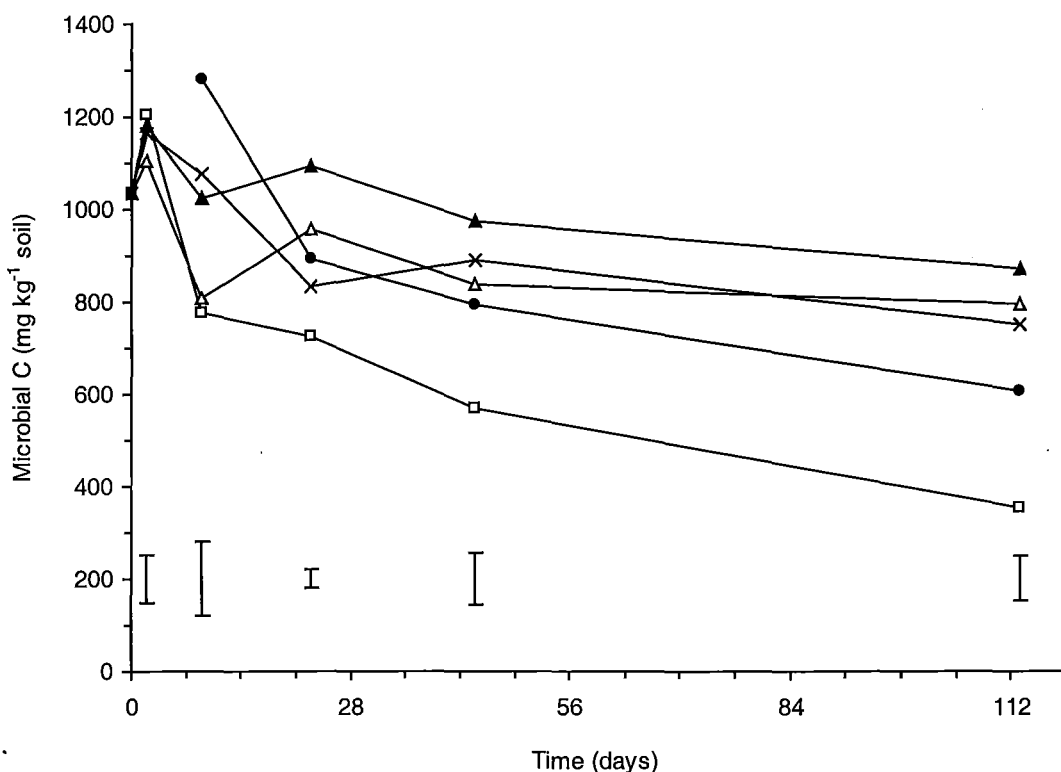


Figure 3.3 Dynamics of soil microbial biomass (mg kg^{-1}). Mean of $n = 3$; bars are L.S.D. $P \leq 0.05$. x Control, Δ Standard DFE, \blacktriangle High DFE, \square Soluble DFE, \bullet Glucose + $\text{NH}_4\text{-N}$.

3.4.3 N mineralisation

Inorganic N contents in the control increased steadily until Day 113 by 130 mg kg^{-1} , equivalent to an average net mineralisation of native soil organic N of $1.15 \text{ mg kg}^{-1} \text{ day}$. This net mineralised N was almost all nitrified (max. 2% $\text{NH}_4\text{-N}$).

DFE application at the standard application rate resulted in soil inorganic N concentrations below those of the control throughout most of the experiment (Figure 3.4). The highest value, measured at Day 113, was still below the $19 \text{ mg kg}^{-1} \text{ NH}_4\text{-N}$ contained in the DFE, indicating that the standard DFE treatment remained in the immobilisation phase until the end of the experiment.

Inorganic N concentrations in the high DFE treatment were higher than in the control by Day 44 and final concentrations at Day 113 corresponded to a net mineralisation of 14% of the organic N contained in the DFE (Figure 3.4).

In the soluble DFE treatment, the maximum $\text{NH}_4\text{-N}$ concentration, equivalent to the applied amount, was recovered at Day 2 (Figure 3.5a). The $\text{NH}_4\text{-N}$ concentration then decreased rapidly to the level of the control treatment (Day 44), with $\text{NO}_3\text{-N}$ concentrations increasing concomitantly (Figure 3.5b). In the glucose treatment, the highest $\text{NH}_4\text{-N}$ concentration was measured at Day 9, and was equivalent to 76% of the $\text{NH}_4\text{-N}$ added. In contrast to the large decrease of $\text{NH}_4\text{-N}$ in the soluble DFE treatment, the decrease in

NH₄-N concentrations by nitrification in the glucose treatment stabilised at a level of about 200 mg NH₄-N kg⁻¹ soil on Day 23. For a short period directly after the effluent application, the NO₃-N concentrations of both the soluble DFE and glucose treatments fell below those of the control (Figure 3.5b).

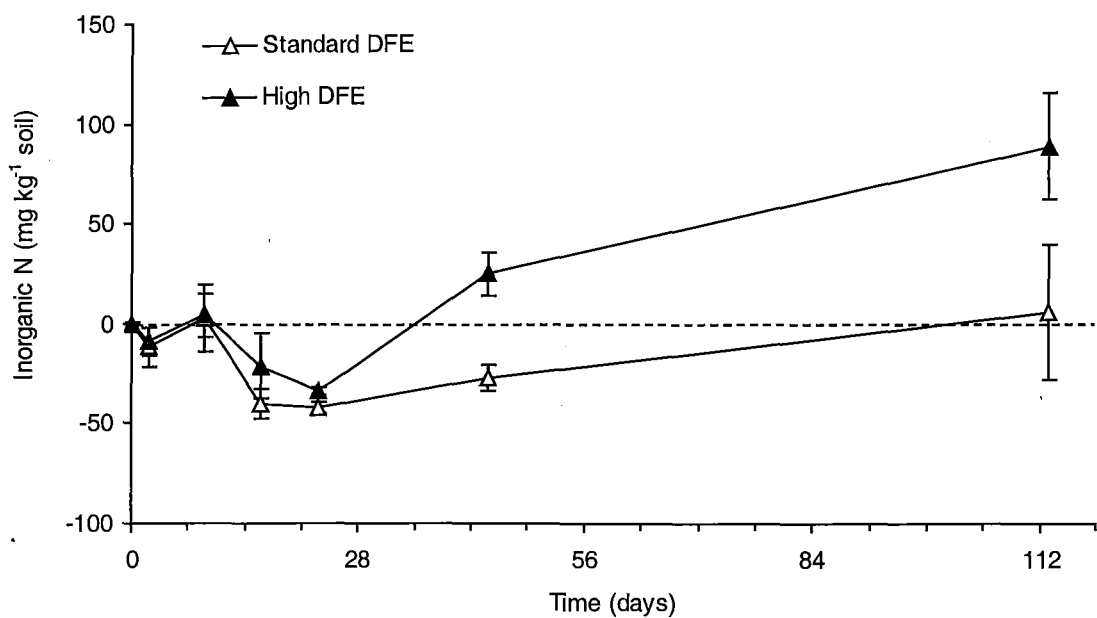


Figure 3.4 Effect of DFE amendments on the dynamics of soil inorganic N (control subtracted, 19 mg kg⁻¹ NH₄-N applied in standard DFE and 52 mg kg⁻¹ NH₄-N in high DFE treatment). Mean of n = 3 ± standard error.

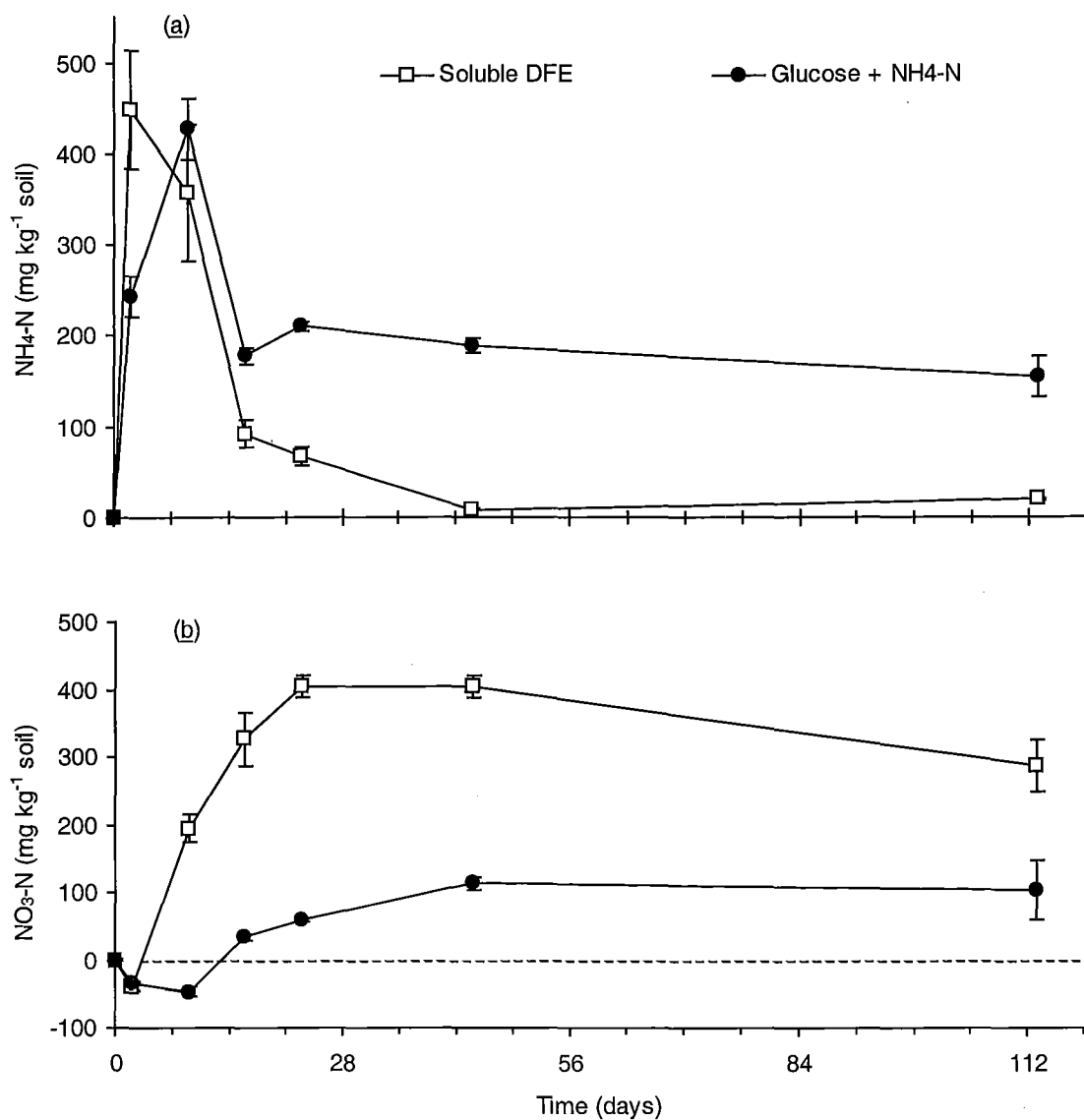


Figure 3.5 Effect of soluble DFE and glucose plus ammonium solution amendments on the dynamics of (a) ammonium N ($\text{NH}_4\text{-N}$) and (b) nitrate N ($\text{NO}_3\text{-N}$), with the control subtracted. Mean of $n = 3 \pm$ standard error.

3.5 Discussion

The decline in C_{mic} over the first 113 days in the control was comparable to data from other soil incubations under comparable conditions (Joergensen *et al.*, 1990; Wu *et al.*, 1993).

3.5.1 Standard and high DFE

Our data suggest that the microbial turnover of DFE differs between loading rates. The standard loading rate resulted in only a brief period of net C mineralisation, no increase in C_{mic} and no NNM, in contrast to on-going net C mineralisation, an increase in C_{mic} and significant NNM in the high DFE treatment. Although water contents were somewhat higher in the high DFE treatment, this is unlikely to be relevant, as both treatments were within the range of optimal water contents for mineralisation. Sparling *et al.* (1981) and Wu *et al.* (1993) have also reported greater percentage mineralisation of substrate-C to CO_2 at higher C loading rates. A possible explanation is that a higher proportion of the substrate makes direct contact with microorganisms when more substrate is applied. Luxury consumption of C with less efficient conversion to cell mass and thus greater CO_2 evolution can also occur if large amounts of substrate are available (Payne, 1970).

The problem of measuring a small amount of DFE-derived CO_2 against high amounts of CO_2 derived from soil organic matter may have contributed to the fall in calculated C recovery in the standard DFE treatment after Day 13. Similar patterns have been reported previously (Liang *et al.*, 1996; Van Kessel *et al.*, 1999).

The net C mineralisation patterns of both DFE treatments were similar to those of cattle manures (Nyamangara *et al.*, 1999), indicating the lower availability of DFE compared to the soluble substrates tested. The low and only gradually changing respiration responses to the standard and high DFE amendments suggest that DFE application is more like a semi-continuous substrate supply to the microbial biomass rather than a pulse of highly available substrate (glucose, soluble DFE). These patterns reflect the complex nature and broad range of C compounds in DFE being successively mineralised. These findings agree with those of Zaman *et al.* (1999) who reported that the mineralisation of DFE results from a sequence of different microbial and extracellular enzyme activities.

The observed N immobilisation after application of effluents with a $C_{org}:N_{org}$ ratio of below 8 is somewhat surprising, as critical C:N ratios of 10-25 have frequently been reported for the turning point between immobilisation and net mineralisation (e.g. Janssen, 1996). However, the concept of a critical C:N ratio is only an approximation that does not consider the quality of the C and N compounds (Jansson and Persson, 1982; Bosatta and Agren, 1985). Due to the intensive turnover in the digestive tract of ruminants, the organic compounds in the DFE can be assumed to have a lower overall microbial availability than plant residues (Floate, 1970), on which the concept of a critical C:N ratio was developed. This result confirms the hypothesis that net N mineralisation from added organic matter is a function of the microbial availability of the added C.

Our results indicate that permitted DFE loading rates should not be based on the impact of DFE on inorganic N pools in the months directly following a single application, but on the long-term effect of regular DFE applications. Considering that the total N loading of the high DFE treatment was about twice as high as permitted annual rates, and that there was no plant uptake during this laboratory incubation, rather small effects of DFE irrigation on soil nitrate concentrations in the months following application onto pasture can be assumed. However, the lack of NNM over the entire 113 days in the standard DFE treatment and the low NNM in the high DFE treatment indicate that continuous application of DFE can result in a gradual accumulation of soil organic N (Barkle *et al.*, 2000). This will continue until a new steady state between supply and mineralisation is reached (e.g. Dittert *et al.*, 1998; Körschens *et al.*, 1998). Although this DFE-derived organic N is not mineralisable in the short-term, it gradually enhances the mineralisable fraction of the total soil organic N and in the long-term will increase the NNM from this pool (Whitmore and Schroeder, 1996). Revised permitted loading rates for DFE should thus be based on nutrient budgets for the soil-plant system that take the gradual increase of mineralisable N_{org} fractions in the soil into account. It might additionally be necessary to develop soil-specific loading rates, as the DFE turnover also differs among soils, with fine-textured soils showing a slower N turnover than coarse-textured ones (Stenger *et al.*, 2001).

3.5.2 Soluble DFE and glucose plus ammonium treatments

Calculation of negative C_{mic} values due to higher concentrations of extractable C in unfumigated than in fumigated samples shortly after glucose amendment has been reported previously (Ladd *et al.*, 1992). The high CO_2 evolution and the rapid reduction in extractable C in the unfumigated samples indicate, however, that the glucose was utilised quickly and microbial growth occurred within 24 h of amendment; this is consistent with other published results (Gregorich *et al.*, 1991; Mary *et al.*, 1993).

We assume that the inhibited nitrification observed in the glucose treatment was due to a nitrification-induced drop in pH. This drop may have been buffered in the soluble DFE treatment by the high pH of the amendment (pH 9.2).

The direct comparison of the soluble DFE and glucose treatments is somewhat hampered as we could not construct a soluble DFE with a C concentration similar to that of the glucose solution. Consequently, further studies would be needed to confirm that the following comparison would be valid with identical concentrations.

The soluble fraction of DFE appeared to have a microbial availability similar to that of glucose. This is somewhat surprising given that there has been ample opportunity for this fraction to be degraded during passage through the digestive system of a dairy cow. The finding suggests that the soluble fraction is being renewed (Whitehead, 1995), possibly by rapid lysis of microbial cells (Lethbridge and Davidson, 1983). Despite having a high microbial availability, the soluble fraction was not dominating the turnover of the whole DFE, as it generally comprises less than 30% of the total DFE-C (Barkle *et al.*, 1994). The net mineralisation pattern of the glucose-C closely follows data from Ladd *et al.* (1992), with an equivalent of 41% of the added C respired after two days. This figure agrees well with the frequently used figure of 40% of glucose-C respired as CO_2 (Paul and Clark, 1989).

The similar overall net C mineralisation of the glucose and the soluble DFE treatments suggested that both were readily available to soil microbes. However, further examination of the CO_2 and C_{mic} data suggests the two substrates were not totally equivalent. Very high respiration rates were measured after a very short lag-phase of only 4 h in the soluble DFE treatment, whereas maximum rates occurred after 14 h in the glucose treatment. This result and the C_{mic} data support the hypothesis that the existing microbial population mineralised a high proportion of the compounds contained in the soluble DFE without adaptation (enzyme production, growth), whereas microbial growth was induced by glucose amendment. This result would seem reasonable considering that microbial populations of grassland soils are more likely to be adapted to the decomposition of moderate amounts of plant and microbial metabolites than to high amounts of pure glucose.

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Chapter Four

Fate of the ^{15}N -labelled faeces fraction of DFE irrigated onto soils under different water regimes

The objective of this Chapter is to:

Investigate the fate of the faecal-N component when DFE is applied onto the soil

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4.1 Introduction

Considerable amounts of N are recycled within dairy farms, as dairy cows excrete as faeces and urine 75-80% of the N they consume (Whitehead, 1995; Ledgard *et al.*, 1996). The faeces and urine excreted in the milking parlour and associated holding yards are diluted with water during the cleaning operation. The resulting dairy farm effluent (DFE) is therefore a very dilute organic effluent, with total solids being less than 1%, and is commonly irrigated onto pasture. Organic N compounds generally make up 60 to 85% of the total N contents of the DFE, with the rest being mainly ammonium as the urea from the urine hydrolyses rapidly (Barkle *et al.*, 1995; Longhurst *et al.*, 2000; TRC, 1990).

The fate of the N is difficult to predict, as numerous processes and pathways are involved in the turnover of the organic N compounds in DFE. A better understanding of the mineralisation-immobilisation turnover (MIT) is required to improve the efficient use of DFE-N and thus reduce the risk of nitrate leaching (e.g. Shepherd *et al.*, 1996). Results from research with stored slurries are not directly applicable to DFE, which is more dilute, contains less ammonium and is applied within one day of excretion. Due to the complexity of and the interactions between the processes, modelling tools are often used to help track and understand the pathways of applied N. A comprehensive model to describe the fate of organic effluents such as DFE applied onto the land is currently under development (Barkle *et al.*, 1995; Barkle *et al.*, 1999). However there is a lack of data on the fate of faecal N applied as DFE.

Labelling animal excreta with ^{15}N has proven to be a valuable tool to elucidate some of the pathways (see the review by Dittert *et al.* (1998)). However, post-excretion ^{15}N labelling of the ammonium fraction has been used in most of these studies. This allows the fate of the applied $\text{NH}_4\text{-N}$ to be investigated, but is not suitable for the organic compounds, which are more important in the medium to longer term. To obtain excreta labelled in both inorganic and organic fractions, an animal must be fed with labelled material. Due to the high costs and time involved in ^{15}N food production, subsequent feeding, and the final excreta collection, this method has rarely been used. In studies where labelled manure or slurry has been used (Sørensen *et al.*, 1994a, 1994b; Sørensen & Jensen, 1998; Thomsen *et al.*, 1997) it has been thoroughly mixed into sieved soil and not irrigated onto the surface as is DFE.

4.2 Materials and methods

4.2.1 Experimental setup

The method of application of an effluent (Sørensen & Jensen, 1998) and the soil structure (e.g. Hassink, 1992; Strong *et al.*, 1998) will influence the fate of effluent-N. To simulate field conditions, we surface-applied DFE with a ^{15}N -labelled faecal fraction onto intact soil cores. Pasture was grown on the soil cores and two water regimes were investigated. The cores were sampled 12 times within a 36-week period at decreasing frequency to obtain time series data on the dynamics of labelled and unlabelled N fractions in soil and in the pasture.

4.2.2 Soil cores

Soil cores (0-210 mm depth) within PVC pipes (143 mm dia. by 220 mm length) were taken from the topsoil of a Te Kowhai soil profile at the Number 1 Dairy, Dairying Research Corporation, Hamilton, New Zealand. The Te Kowhai silt loam is described as a Typic Orthic Gley (Hewitt, 1992, New Zealand Classification) or a Typic Ochraqualf (Soil Survey Staff, 1990, USA classification). The particle size distribution in the topsoil was 40% clay, 46% silt and 14% sand; the pH was 6.6. The cores were subdivided into an upper layer (U, 0-100 mm) and a lower layer (L, 100-210 mm) prior to analysis. Some basic soil properties of these layers are given in Table 4.1.

Table 4.1 Some properties of the two soil compartments (U = upper layer, L = lower layer, D = dry treatment, W = wet treatment). Porosity = $(1 - \text{bulk density/particle density})$, C_t = Total C, N_t = Total N.

	Bulk density (g cm ⁻³)	Porosity (-)	C_t (%)	N_t (%)
U-D	0.85	0.64	8.22	0.65
L-D	1.04	0.58	6.63	0.41
U-W	0.84	0.65	8.22	0.64
L-W	1.04	0.58	6.33	0.43

The cores were hand-carved from the soil into the PVC pipes using the method of Cameron *et al.* (1992). Plates of 8-mm PVC with five 12-mm holes were attached to the base of the pipes containing the cores. Each water treatment was replicated 15 times.

4.2.3 Effluents

The labelled faeces were produced by feeding hydroponically grown ¹⁵N-labelled grass and clover to a dairy cow over a three-day period. This procedure ensures that both the inorganic and the predominant organic compounds in the faeces are labelled (Dittert *et al.*, 1998; Sørensen & Jensen, 1998). As the experiment was aimed at investigating explicitly the N turnover of the faecal fraction of DFE, the labelled faeces (mean ¹⁵N 2.95 atom%) were mixed with water and unlabelled urine in proportions to that commonly found in DFE (Table 4.2). A small amount of faeces had been added to the urine to encourage hydrolysis of urea. The urine contained 4152 mg TKN l⁻¹, 3589 mg NH₄-N l⁻¹ and 44 mg urea-N l⁻¹ when it was mixed with the labelled faeces. The resulting effluent had a pH of 8.7.

Table 4.2 Properties of the faeces, the constructed DFE, and 0.5-mm and 0.2- μ m filtered samples. Mean \pm standard deviation of $n = 3$. TOC: Total organic C, TKN: Total Kjeldahl N, Organic N calculated: $N_{org} = TKN - NH_4-N$. Mean \pm standard error of the difference.

	Units	Faeces	Constructed DFE	0.5-mm filtered	0.2- μ m filtered
TOC	(g l ⁻¹)	ND	24.40 \pm 3.60	11.47 \pm 1.28	1.98 \pm .23
TKN	(mg l ⁻¹)	4544 \pm 226	1864 \pm 94	1132 \pm 235	416 \pm 75
NH ₄ -N	(mg l ⁻¹)	685 \pm 142	439 \pm 27	298 \pm 34	211 \pm 41
N _{org}	(mg l ⁻¹)	3860 \pm 266	1425 \pm 98	834 \pm 238	204 \pm 85
TOC/TKN	(-)	ND	13.1	10.2	4.8
TOC/N _{org}	(-)	ND	17.1	13.8	9.7
TK ¹⁵ N	(atom%)	2.95 \pm 0.12	2.48 \pm 0.07	2.18 \pm 0.08	1.32 \pm 0.09
	(mg l ⁻¹)	134.0 \pm 8.7	46.3 \pm 2.6	24.6 \pm 5.2	5.5 \pm 1.1
¹⁵ NH ₄ -N	(atom%)	2.16 \pm 0.11	1.23 \pm 0.02	0.97 \pm 0.02	0.77 \pm 0.04
	(mg l ⁻¹)	14.8 \pm 3.1	5.4 \pm 0.3	2.9 \pm 0.3	1.6 \pm 0.3
¹⁵ N _{org}	(atom%)	3.09 \pm 0.16	2.87 \pm 0.07	2.61 \pm 0.08	1.89 \pm 0.10
	(mg l ⁻¹)	119.2 \pm 7.1	40.9 \pm 1.2	21.9 \pm 2.3	3.9 \pm 0.7

When DFE is irrigated onto the soil surface the particulate material is filtered out by surface straining (Barkle *et al.*, 1999). To be able to understand the physical distribution of the faecal fraction of the DFE when it is surface-irrigated onto the soil, the various size fractions and their ¹⁵N enrichment must be known. To investigate this filtration effect, DFE was passed through a 0.5-mm Endecotts sieve, or a 0.2- μ m pre-flushed Sartorius cellulose filter and the filtrates analysed for ¹⁵N fractions (Table 4.2).

4.2.4 Treatments

To minimise any leaching losses from the cores, a 17 mm depth of DFE was applied over five hours on Day 1, corresponding to about half the core's available water storage. The effluent application resulted in a total N loading of 318 kg ha⁻¹, 75 kg ha⁻¹ of it NH₄-N. The two water treatments investigated were a dry treatment (D, target soil water content 30%) and a wet treatment (W) where a water table was maintained at approximately 17 cm from the soil surface using a shallow water-filled tray. In the dry treatment, evapotranspiration losses were replenished every two to three days after an initial drying period of 16 days. The wet treatment maintained the water content at about 55%. The soil cores were held in a controlled environment room at a constant temperature of 18°C.

4.2.5 Analysis of effluent, plant, soil and leachates

Samples for the investigation of N dynamics were taken by extraction of a soil plug (17 mm dia.) from each of the 30 cores, except for the final destructive sampling at Day 254. Samples were taken at Day 0, and immediately following effluent application on Day 1, then subsequently on Days 4, 7, 11, 17, 30, 51, 78, 108, 150, and 191. At each sampling, the plugs from all 15 cores of each treatment were bulked prior to analysis to ensure that there was sufficient labelled N in the sample for detection. The cavities formed by soil extraction were filled with tightly fitting PVC tubes. The soil samples were sieved and roots removed for separate analysis. Pasture grown on the topsoil cores was cut and analysed six times, at Days 30, 51, 78, 150, 191, and 254. At the final sampling (Day 254), pasture, stubble, root, litter, and remaining effluent on the soil surface were determined after oven drying at 60°C for at least 24 h. The water and soil sediments in the shallow water tray used for maintaining the water table in the wet treatment were also collected and analysed for labelled N.

Total N in soil and plant material, as well as total C in soil, were measured in finely ground samples using a Dumas Elemental Analyser (Europa Scientific ANCA-SL). For ^{15}N analysis it was interfaced to a stable isotope mass spectrometer (Europa Scientific Tracermass, Crewe, U.K.). Kjeldahl N was measured by microdigestion followed by microdistillation and titration (Bergersen, 1980). NH_4^+ and NO_3^- were extracted with 2 M KCl solution for 1 h with a soil:solution ratio of 1:5 (mass:volume) using an end-over-end shaker. NH_4^+ and NO_3^- were measured using standard auto-analyser techniques (Blakemore *et al.*, 1987). Total C in the effluent was measured using the acid digestion method of Tinsley III (Kalembasa & Jenkinson, 1973). Microbial biomass measurements were made using the chloroform-fumigation and extraction method (CFEM) (Brookes *et al.*, 1985; Vance *et al.*, 1987). It was assumed that 42% of the microbial C, $k_{\text{EC}} = 0.42$; (Sparling *et al.*, 1990) and 45% of the microbial N, $k_{\text{EN}} = 0.45$ (Jenkinson *et al.*, 1985) are extracted by this method. Total C was measured on 0.2- μm filtered samples using an automated C analyser (Shimadzu, TOC 5000) by combustion followed by non-dispersive infrared detection of CO_2 gas.

4.3 Results

4.3.1 Effluent

The $\text{NH}_4\text{-N}$ fraction of the faeces had a lower ^{15}N abundance (2.16 atom%) than the N_{org} fraction (3.09 atom%) (Table 4.2). The subsequent mixing of the labelled faeces (predominantly N_{org}) with unlabelled urine (predominantly $\text{NH}_4\text{-N}$) and water resulted in more than 90% of the ^{15}N being in the organic N fraction, with ^{15}N abundances of 1.23 atom% in the $\text{NH}_4\text{-N}$ and 2.48 atom% in the N_{org} fractions of the constructed DFE.

Filtering through the 0.5-mm and 0.2- μm filters decreased the N_{org} component of the DFE, to 58% and 14% of the unfiltered N_{org} value, respectively. Not only the N_{org} content, but also its ^{15}N abundance dropped to 91% and 66% of that of the unfiltered DFE. Hence, ^{15}N was not distributed homogeneously throughout all fractions of N_{org} . $\text{NH}_4\text{-N}$ was not entirely in the dissolved phase, as the dissolved (0.2- μm)

sample had only 48% of the $\text{NH}_4\text{-N}$ content of the unfiltered DFE. The ^{15}N abundance of this pool also decreased with filtration to 63% of the value in the unfiltered DFE. Hence, disproportionally more of the labelled $\text{NH}_4\text{-N}$ was thus associated with the larger material in the DFE.

4.3.2 Pasture-N uptake

At all cuts, pasture yield was higher in the wet than in the dry treatment (Table 4.3). For the first two cuts, this coincided with lower N concentrations. Subsequently, N concentrations were higher in the wet treatment. The recovery of applied ^{15}N was higher in the wet treatment, at the end of the experiment totalling 5.1% compared to 2.4% in the dry treatment.

Table 4.3 Yield and N removal in the dry and wet treatments at six cuts. ^{15}N uptake rates are given for the period between cutting dates.

Cutting day	Dry weight	Plant N	¹⁵ N excess in plant material		¹⁵ N uptake rate	
			Period		Cum.	
		(g m ⁻²)	(%)	(atom%)	(% appl. ¹⁵ N)	
Dry						
30	60	2.53	0.145	0.33	0.33	73.0
51	29	2.32	0.146	0.15	0.47	47.4
78	8	2.26	0.214	0.06	0.53	14.6
150	33	2.18	0.102	0.11	0.64	10.3
191	83	2.41	0.146	0.44	1.08	71.7
254	193	1.81	0.261	1.36	2.44	145.0
Wet						
30	144	1.95	0.200	0.84	0.84	187.7
51	63	1.93	0.236	0.42	1.26	136.0
78	37	2.27	0.279	0.35	1.61	87.8
150	239	2.56	0.111	1.01	2.63	94.5
191	188	2.68	0.046	0.34	2.97	55.8
254	471	2.17	0.141	2.14	5.10	228.1

4.3.3 Total and labelled inorganic N

The changes in total and labelled ammonium and nitrate contents from Day 0 are presented in Figures 4.1 to 4.3. In the dry upper layer, soil inorganic N showed little change after Day 1 (Figure 4.1). In the wet treatment, plant-available N from applied $\text{NH}_4\text{-N}$ and net N mineralisation (NNM) surpassed the demand of the pasture (Table 4.3), hence soil inorganic N accumulated (Figure 4.2). In the dry treatment, plant N uptake was only 33% of that of the wet treatment and soil inorganic N concentrations were at or below

initial values throughout most of the experiment. The inorganic N and pasture N summed to an equivalent of 290 kg N ha⁻¹ in the wet treatment and 87 kg in the dry treatment. At any time only a very small proportion of the applied ¹⁵N was recovered in inorganic N (D 1.6%, W 1.0%, Figure 4.3).

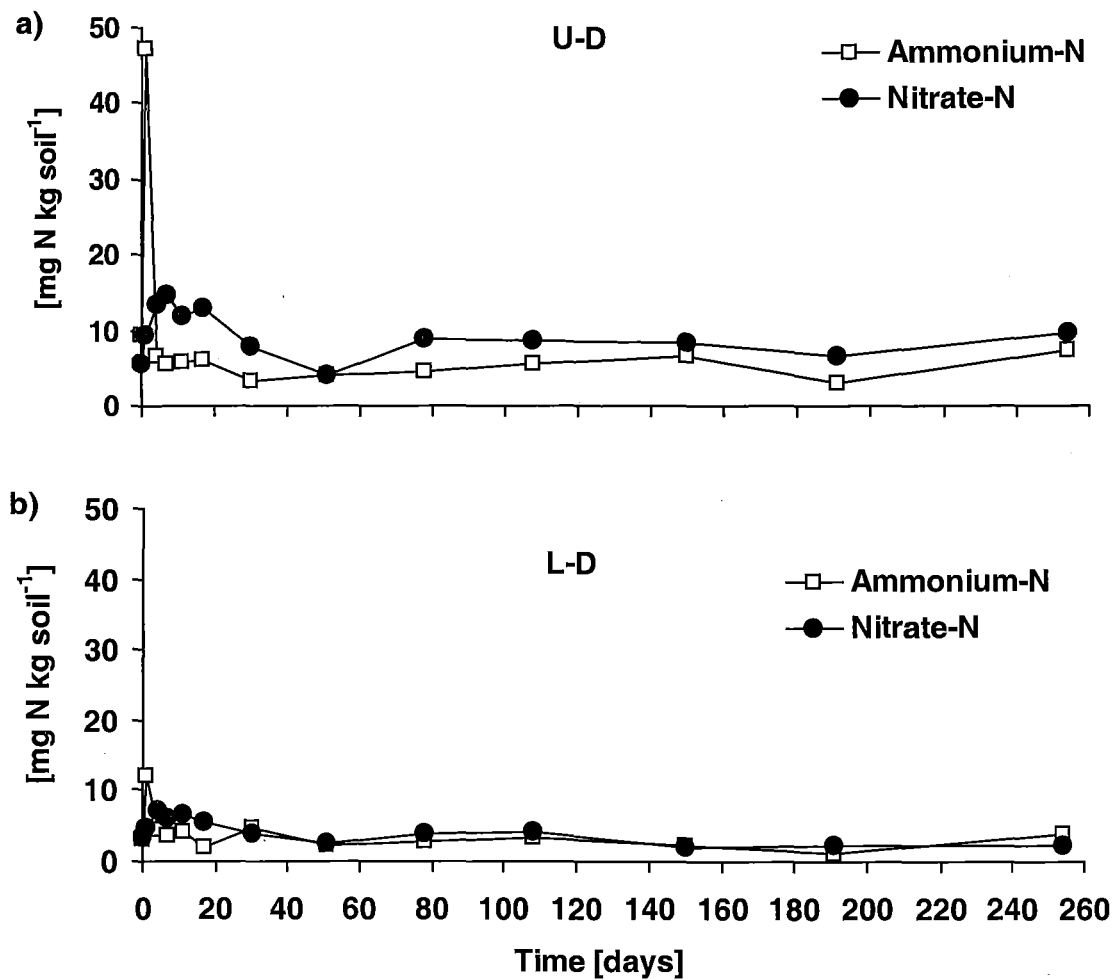


Figure 4.1 KCl-extractable NH₄-N and NO₃-N. (a) upper layer, dry treatment (U-D), (b) lower layer, dry treatment (L-D).

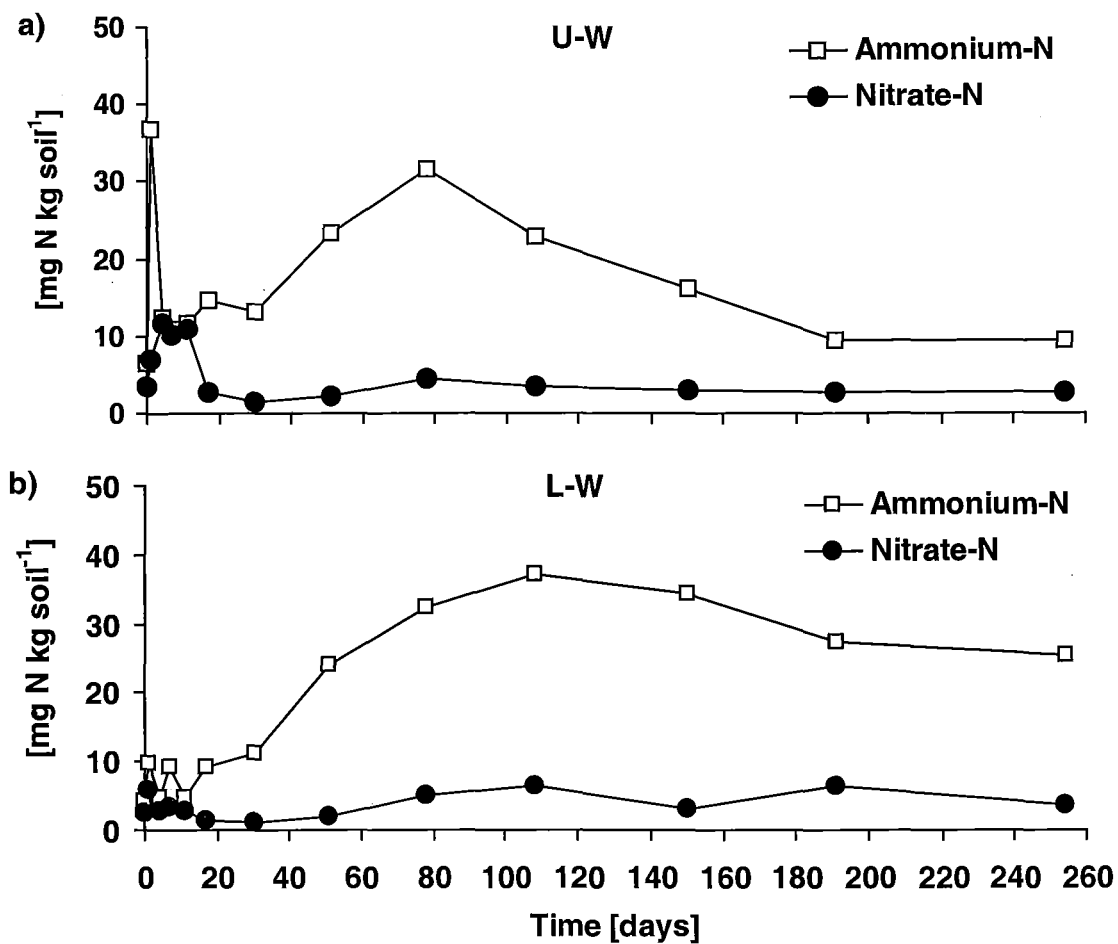


Figure 4.2 KCl-extractable $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$. (a) upper layer, wet treatment (U-W), (b) lower layer, wet treatment (L-W).

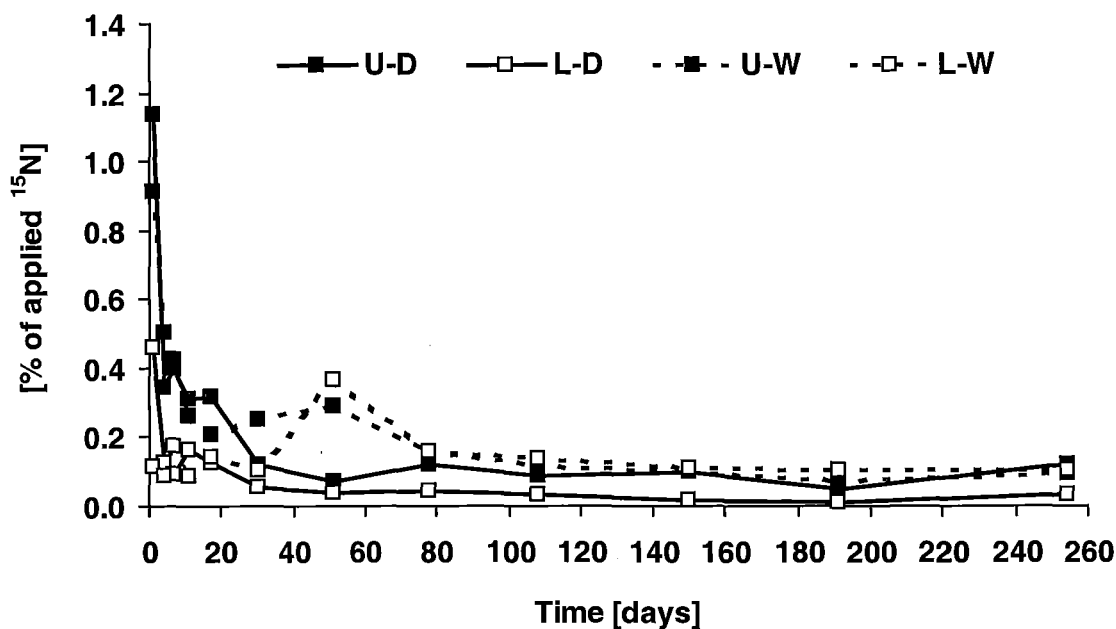


Figure 4.3 KCl-extractable inorganic ^{15}N ($^{15}\text{NH}_4\text{-N}$ + $^{15}\text{NO}_3\text{-N}$) as percentage of the applied ^{15}N .

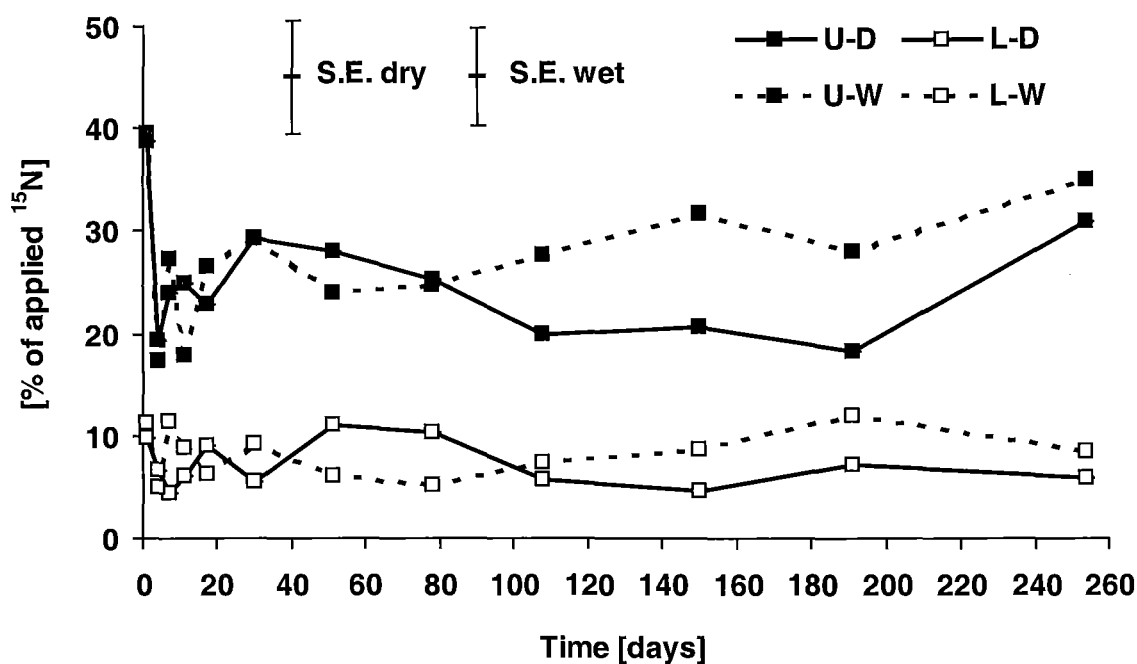


Figure 4.4 Dynamics of ^{15}N in soil organic matter as percentage of the applied ^{15}N ($N_{\text{org}} = N_t - \text{inorganic N}$), S.E. mean standard error of the wet and dry treatment, respectively.

4.3.4 ^{15}N -labelled soil organic N

In the upper layer, the highest recovery of ^{15}N in soil organic N (39% in U-D and 40% in U-W) was found at Day 1 (Figure 4.4). In both treatments, ^{15}N concentrations dropped markedly from Day 1 to Day 4 and then fluctuated between 17% and 35%. About 10% of the applied ^{15}N was measured in the lower layer of both treatments at Day 1.

4.3.5 Recovery of ^{15}N at the end of the experiment

The recovery of the ^{15}N in soil fractions was 37.1% in the dry treatment and 43.6% in the wet treatment (Table 4.4), of which approximately 95% was in the organic N fraction. In both treatments most of the $^{15}\text{N}_{\text{org}}$ was found in the upper layer, 85% in U-D and 80% in U-W, and only very small amounts of ^{15}N (< 0.5%) in inorganic N ($\text{NH}_4\text{-N} + \text{NO}_3\text{-N}$). Labelled N in the soil microbial biomass (N_{mic}) was very low in the lower layer, but reached 1.2% of the ^{15}N applied in U-D and 0.8% in U-W. Compared to the recovery in harvested pasture (2.4% in D, 5.1% in W), a high proportion of ^{15}N was recovered in the stubble of both treatments (Table 4.4). In the dry treatment, this was mainly due to the higher dry matter yield of the stubble, in the wet treatment to higher ^{15}N enrichment of the stubble. The higher proportion of ^{15}N in the root system of the dry treatment was mainly caused by a 70% higher root mass. Plant litter collected from the soil surface accounted for 1.3% in the dry and 1.5% in the wet treatment. The higher ^{15}N enrichment in the litter than in harvested plant material suggests that this material may have become contaminated with ^{15}N from effluent still on the soil surface at Day 254. The effluent remaining on the surface made up 9.9% of the applied ^{15}N in the dry and 13.5% in the wet treatment. During the DFE application very small amounts of ^{15}N were leached from the soil cores (Table 4.4). The sediment and water in the trays of the wet treatment contained a maximum of 0.2% of the applied ^{15}N . Overall ^{15}N recoveries were 71.5% in the wet treatment and 58.4% in the dry treatment.

Table 4.4. Balance of the ^{15}N recovered after 254 days in the soil, plant material, leachates, and effluent remaining on the soil surface ($N_{\text{org}} = N_{\text{t}} - \text{NH}_4\text{-N} - \text{NO}_3\text{-N} - N_{\text{mic}}$).

Fraction	Recovery of ^{15}N applied (%)					
	D			W		
	U	L	Sum	U	L	Sum
Soil						
NH ₄ -N	0.1	0.0	0.1	0.1	0.1	0.2
NO ₃ -N	0.1	0.0	0.1	0.0	0.0	0.0
N _{org}	29.8	5.3	35.1	34.2	8.3	42.5
N _{mic}	1.2	0.6	1.8	0.8	0.1	0.9
Subtotal	31.2	5.9	37.1	35.1	8.5	43.6
Plant						
Shoots			2.4			5.1
Stubble			1.9			4.8
Roots			3.7			1.6
Litter			1.3			1.5
Subtotal			9.3			13.0
Leachates						
Effluent			2.1			1.3
Water table			-			0.1
Sediment			-			0.1
Subtotal			2.1			1.5
Remaining effluent			9.9			13.5
Total recovery			58.4			71.5

4.4 Discussion

Few other studies have investigated the fate of $^{15}\text{N}_{\text{org}}$ from ruminant manures (Sørensen *et al.*, 1994a, 1994b; Sørensen & Jensen, 1998; Thomsen *et al.*, 1997). This group, working with labelled sheep faeces incorporated into lysimeters planted with cereal crops and ryegrass, reported total ^{15}N recoveries between 70% and 90%. With 58% in the dry and 72% in the wet treatment, our recoveries were somewhat lower.

One factor contributing to the difference in recovery was probably the application method. A high proportion of the surface-applied ^{15}N was not readily accessible for plant uptake and prone to gaseous and physical losses. Volatilisation losses are likely to have been higher in our experiment as our dairy cow faeces had a much higher $^{15}\text{NH}_4\text{-N}$ content (10% of total ^{15}N) than their sheep faeces (< 1%). In contrast to the field experiment of Sørensen *et al.*, (1994b), the lack of heavy rain and drying/rewetting cycles in our controlled environment prevented the ^{15}N remaining on the surface from being washed into the root zone.

The losses from the surface were also reflected in lower plant uptake. The barley crop of Sørensen *et al.* (1994b) took up 16-17% of the labelled manure N, compared to 9 and 13% in the dry and wet treatment, respectively. Another reason for the difference in plant uptake may be that the mineralisation in our intact, clayey soil cores was retarded (Hassink, 1992; Sørensen & Jensen, 1998; Strong *et al.*, 1998) compared to the much coarser, sieved, soil-quartz sand mixtures used in the other studies. This argument is also supported by the fact that the highest daily ^{15}N plant uptake rates were measured during the last period.

The aim of this study was to measure the ^{15}N dynamics in various soil and plant fractions after the irrigation of a ^{15}N -labelled faecal fraction to improve understanding of the complex turnover processes. While mixing of the faecal fraction (predominantly a source of slowly available organic N) with urine (mainly immediately available inorganic N) was necessary to simulate the application of DFE, the results do not necessarily reflect the turnover of the two fractions when applied separately.

The underlying assumption in ^{15}N experiments is that the small, labelled portion of an amendment directly reflects the dynamics of its large unlabelled portion. This is only fulfilled if all N fractions of the amendment are uniformly labelled. However, our results show considerable heterogeneity at two levels of the ^{15}N labelling that complicates the calculation of the total turnover of the faecal N on the basis of ^{15}N results.

Firstly, the ^{15}N -labelled faeces contained two distinct fractions ($^{15}\text{NH}_4\text{-N}$, $^{15}\text{N}_{\text{org}}$), that differed in ^{15}N enrichment, similar to the result of Sørensen *et al.*, (1994a) for labelled sheep faeces. Depending on the length of the labelling period, they reported generally lower (1.07-2.93 atom%) $^{15}\text{NH}_4\text{-N}$ enrichments than those of the total N (1.14-3.55 atom%). They concluded that endogenous N of the digestive tract (microbial N, secretions) contributed more to the $\text{NH}_4\text{-N}$ than the N_{org} in the faeces. This non-uniformity can be neglected when $\text{NH}_4\text{-N}$ contributes only a tiny proportion to total N, as in their study, but it complicates the interpretation of our ^{15}N data, as $\text{NH}_4\text{-N}$ represented 24% of the total N and 9.6% of the ^{15}N in the DFE. Nevertheless, the overall recovery is indisputable and thus quite often only the ^{15}N enrichment of total N is reported in other published studies, even if the effluent contains significant amounts of $\text{NH}_4\text{-N}$, e.g. Bergström & Kirchmann, (1999).

Secondly, the dominant $^{15}\text{N}_{\text{org}}$ fraction itself was not labelled homogeneously. Assuming that the smaller size fraction is the easily decomposable fraction with a lower $^{15}\text{N}_{\text{org}}$ enrichment (Sørensen *et al.*, 1994a), then using the average enrichment underestimates the turnover of faecal N. Additionally, the physical fractionation of labelled and unlabelled compounds when DFE is irrigated onto the soil exacerbates the heterogeneity.

Two results indicate that the dynamics of the ^{15}N -labelled fractions of DFE ($^{15}\text{NH}_4\text{-N}$, $^{15}\text{N}_{\text{org}}$) do not properly reflect the dynamics of the unlabelled fractions. Firstly, the analysis of the different size fractions showed the coarsest fractions had the highest enrichment. Consequently, relatively more $^{15}\text{N}_{\text{org}}$ than unlabelled N_{org} was filtered out during the infiltration. From the total recovery of about 53% in soil and leachate immediately after application, it can be deduced that about 47% of the ^{15}N must have been left on the surface or lost immediately by gaseous losses (NH_3 , N_2O , N_2). Initial gaseous losses were presumably small, as $^{15}\text{NH}_4\text{-N}$ was low (see below) and at least 10% of the applied ^{15}N could still be measured in DFE remaining on the soil surface at the end of the experiment.

Secondly, the recovery of labelled $\text{NH}_4\text{-N}$ in the KCl soil extracts indicated inconsistency between labelled and unlabelled material. Immediately after effluent irrigation, on average 44% of the unlabelled $\text{NH}_4\text{-N}$ was recovered, compared to only 11% of the $^{15}\text{NH}_4\text{-N}$. This would leave 89% of the applied $^{15}\text{NH}_4\text{-N}$ remaining on the surface. This result is consistent with the higher ^{15}N enrichment (Table 4.2) of the $\text{NH}_4\text{-N}$ associated with the larger material filtered out on the surface. The decrease in ammonium concentration with filtration indicates adsorption of ammonium onto the particulate or non-dissolved fraction of the DFE. Concomitantly, there was a decrease in ^{15}N abundance (Table 4.2). As both the $^{15}\text{NH}_4\text{-N}$ and $^{15}\text{N}_{\text{org}}$ were derived from the faeces, the labelled ammonium may have been more closely associated with the particulate material than the unlabelled ammonium from the amended urine.

Apparently, higher proportions of the ^{15}N -labelled N_{org} and $\text{NH}_4\text{-N}$ fractions than of the respective unlabelled fractions were left on the surface. Consequently, the ^{15}N losses from the surface probably overestimated the losses of unlabelled N from the surface.

Rapid downward movement of DFE by preferential flow occurred as well during the infiltration process. This is indicated by the small amount of ^{15}N that leached during irrigation when the water content of the cores was well below saturation.

The reason for the apparent drop in $^{15}\text{N}_{\text{org}}$ between Days 1 and 4 remains unclear as no corresponding increase in any other measured ^{15}N fraction was found. Although N losses due to denitrification have been reported after application of cattle slurries, losses of about 20% of the applied ^{15}N are unlikely (e.g. Christensen, 1983; Clayton *et al.*, 1997; Jarvis *et al.*, 1994; Loro *et al.*, 1997). In both treatments, the recovery of ^{15}N in $^{15}\text{N}_{\text{org}}$ fluctuated around 35% after Day 4. The scatter observed in the $^{15}\text{N}_{\text{org}}$ time series is mostly due to analytical variation in total N and ^{15}N measurements. Although the mean coefficients of variation of these measurements were very small (below 1.0% and 0.6%, respectively) due to the low amounts of ^{15}N amended, the resulting mean standard error for the calculated ^{15}N amount is 5.5% (D) and 4.8% (W) of the amendment. Another contributing factor is the spatial variability that could not be overcome by the sampling procedure. To keep the soil cores as intact as possible, the sample volume at the 12 samplings prior to the destructive sampling had to be small (1.4% of the soil volume per sampling).

As most $^{15}\text{NH}_4\text{-N}$ and a high proportion of the coarser $^{15}\text{N}_{\text{org}}$ fractions were left on the surface, we assumed the ^{15}N enrichment of the N_{org} component of the 0.5-mm-filtered sample best represented the DFE that infiltrated the soil. This value was then used to calculate the contribution of DFE-N to all plant N fractions and soil inorganic N. The calculated N derived from DFE was 28 of the 147 kg N ha⁻¹ in the dry, and 40 of the 346 kg N ha⁻¹ in the wet treatment. These values are equivalent to 9 and 13% of the

applied DFE-N. The difference in total available N between treatments was due to an enhanced contribution of faecal N to the plant-available pool during the first 50 days in the wet treatment, but not in the dry treatment. Assuming that the contribution of urine-N to the plant-available pool was similar in both treatments, the amounts of N derived from soil organic matter must have been considerably higher in the wet treatment. The component of the mineralised N that was not taken up accumulated as $\text{NH}_4\text{-N}$ in the wet treatment, since nitrification was restricted at the high water-filled pore volumes of this treatment (> 85%).

Due to the effect of non-uniformly labelled faeces, which was exacerbated by the filtration of DFE on the soil surface, simplifying assumptions had to be made to calculate the turnover of the total faecal fraction based on ^{15}N results. To address this problem, alternatives include amending labelled faecal material to inert quartz sand in incubation experiments (Sørensen *et al.*, 1994a). This may help to identify the sources of soil inorganic ^{15}N . Using a curve-splitting procedure on the time series of soil inorganic ^{15}N contents should allow identification of distinct pools ($^{15}\text{NH}_4\text{-N}$, readily and slowly mineralisable $^{15}\text{N}_{\text{org}}$ fraction) from which the soil inorganic ^{15}N is derived. However, as all interactions between soil and amendment are excluded, it has yet to be shown that results obtained in such experiments properly reflect the turnover in soil-plant systems. Another option is using extraction and filtration to separate ammonium and organic fractions of the faeces and evaluate the fate of ^{15}N separately.

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Chapter Five

Leaching of particulate organic C from land-applied DFE

The objectives of this Chapter are to:

Measure the filtration behaviour of the particulate fraction of DFE applied onto soil cores

Develop a transport/filtration model capable of describing the observed behaviour

Parameterise the model and compare the simulated to the measured results

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5.1 Introduction

Dairy farm effluent is a very dilute organic slurry composed of dairy cow faeces and urine mixed with water that is produced from the wash-down of the milking parlor and accompanying holding yards. The effluent's exact composition is highly variable and depends on animal age, feed type, pasture quality, soil nitrogen levels, climate, and other factors. The total solids content is very low, typically less than 1% (Vanderholm, 1984; Barkle *et al.*, 1994). Nitrogen is present in the effluent as ammonium-N, urea-N, and in organic compounds. Typically, 60-85% of the N is organic (TRC, 1990; Barkle *et al.*, 1995; Selvarajah, 1996). The organic compounds in the effluent can be classified by particle size. Material passing a 0.2- μm filter is defined as dissolved. The remainder, which is particulate, constitutes between 55% and 80% of the total organic nitrogen present in dairy farm effluent (Macgregor *et al.*, 1979; Barkle *et al.*, 1994).

Leaching studies (Cooke *et al.*, 1979; Macgregor *et al.*, 1979; Singleton *et al.*, 2001) on drained soils using dairy farm effluent found that organic-N, including the particulate fraction, can be a potential pollutant to surface waterways and shallow ground-water systems. In the study by Macgregor *et al.* (1979) dairy farm effluent was applied in spring onto a drained silt loam pasture. Of the resulting N leached, 57% was in an organic-N form, with only 5% in a nitrate-N form. Similar results were found by Cooke *et al.* (1979) for effluent applications made in late winter and late spring, where 65% and 76%, respectively, of the total nitrogen leached was organic-N. Cooke *et al.* (1979) further characterised the leachate into dissolved and particulate fractions, which showed 72% of the organic-N to be particulate in the winter event and 53% in the spring application.

Using a poorly drained silt loam soil, the same effluent type was irrigated over a 2-year period onto lysimeters with various drainage treatments installed (Brown and Barkle, 1996; Singleton *et al.*, 2001). Averaged data over all seasons and drainage treatments showed that 80% to 90% of the N leached was in an organic form, with less than 13% as nitrate. Size fractionation of this leached material showed that between 60-70% of the N leached was particulate, and approximately 70% of the C in the leachate was also in this undissolved form.

Geohring *et al.* (1997) studied the preferential movement of liquid dairy cow manure applied onto a drained fine sandy loam (mixed mesic Aeric Ochraqulf) pasture in northern New York state. They sampled the drainage water using grab sampling techniques from tile drains installed in an experimental field receiving liquid manure. Within 40 min of commencement of the subsequent clean-water irrigation event, the drainage water had discoloured, and faecal coliform and nutrient contamination had occurred. They concluded that preferential flow processes can have important implications on the fate and rapid transport of nutrients and pathogens from the application of manures. Evans and Owens (1972), Dean and Foran (1992), and Fleming and Bradshaw (1992) have also reported that the application of liquid manure to drained fields results in a rapid increase in the concentration of nutrients and bacteria in tile drainage attributable to soil macropores. Other studies (Davies, 1969; ARC, 1976) in which different types of organic effluents were applied onto poorly drained soils found similar organic contamination of the drainage leachate. In guidelines for the application of organic effluent, O'Callaghan *et al.* (1973) highlighted the risk of leaching high BOD (Biological Oxygen Demand) and N compounds when manure is spread onto land where the moisture content exceeds field capacity. These studies all highlight the need

to consider organic matter as a potential pollutant to the receiving environment when organic effluents are applied onto some soils.

The main physical mechanisms involved in a filtration process are surface straining, interception, transport processes (sedimentation and diffusion), and attachment mechanisms (Haarhoff and Cleasby, 1991). Surface straining or surface screening is the most obvious capture mechanism for particles that are too large to pass through the soil pores at the surface. When this same screening phenomenon occurs within the soil medium itself, the process is referred to as interception. Given ideal spherical grains the soil pores can capture particles larger than about 15% of the grain-size diameter (Haarhoff and Cleasby, 1991). The size of the pore openings will, however, be both larger and smaller than this idealised representation because soil particles are obviously of various sizes and shapes. The question arises also as to how much a single pore can contribute to the quality of the total leachate; one large macropore may, in fact, totally dominate the quality of the leachate. Transport processes that may affect filtration indirectly include sedimentation, diffusion and attachment. When pore velocities are lowered, particles may settle out via sedimentation. Diffusion may transport material from mobile flow zones to immobile regions, thereby effectively filtering out the material. Finally, attachment (electrostatic attraction, Van der Waal's forces, and adsorption) may also remove particles.

This work regarding C leaching from land-applied effluent forms part of a larger project about the hydrological and nutrient loadings that provide a practical rate of dairy farm effluent disposal with an acceptably low pollution risk. The larger project includes the development of a complex simulation model to allow various land-based effluent treatment options to be evaluated (Barkle *et al.*, 1995). Obviously an important part of such a simulation is a realistic sub-model for the transport and leaching behaviour of particulate organic matter in the soil. Although models for the deep-bed filtration of colloids in groundwater within fractured porous media have been developed (Ibaraki and Sudicky, 1995) and similarities exist with bacterial filtration models (Reddy and Ford, 1996), no suitable simulation model exists to describe the movement and filtration of organic material of differing sizes in the soil. This Chapter proposed a model that is capable of reproducing the experimental results obtained for the leaching of particulate organic matter and could, therefore, be expected to be useful for predicting movement and filtration of effluent of various sizes in the soil.

5.2 Materials and methods

5.2.1 Size characterisation of the effluent

A typical effluent was prepared by mixing fresh dairy cow faeces and urine with water. Replicates of the effluent were filtered through a single flushed filter from either an Endecotts wire mesh filter (2 mm, 500- μ m, 105- μ m, and 38- μ m), a Whatman quantitative cellulose filter (grade 52, 7- μ m retention size, grade 50, 2.7- μ m retention), or a Sartorius AG cellulose acetate filter (0.2- μ m retention size) to separate it into the arbitrary size ranges. A separate effluent sample was used for each filter, though all samples were taken from the same batch of effluent. The amount of C removed by each filter was determined by the difference between the applied and the filtrate (material passing the filter) concentrations. This was

done to avoid problems associated with washing material from the filters, particularly the cellulose papers. All filter papers were initially flushed with 50 ml of deionised water. Water blanks were used to correct for any C leaching from the cellulose filters.

The organic C content in all size fractions in the effluent, except for 0.2- μm fraction, was determined by an acid dichromate method based on that of Tinsley III (Kalembasa and Jenkinson, 1973). In this method, the organic matter is oxidised under reflux with excess acid dichromate reagent, and the residual dichromate is then estimated by back-titration with ferrous ammonium sulphate. The C in the filtrate from the 0.2- μm filter was determined using an automated C analyser (Shimadzu, TOC 5000) that uses combustion, followed by a nondispersive infrared detection of CO_2 gas. All C measurements made with the acid dichromate method were multiplied by 1.19 to enable direct comparison to the measurements made by the C analyzer (Wu *et al.*, 1990).

5.3 Application onto undisturbed soil cores

All cores used in the study were pre-wet to field capacity by applying a 30-mm depth of water as an instantaneous slug. The cores were then allowed to drain for 24 hours before the effluent or control treatments were applied. During this wetting-up phase some subsoil cores did not allow water to infiltrate and produced no leachate. The experimental treatments were, however, still applied onto these cores for completeness of the experiment.

The same batch of effluent was applied as a 30-mm instantaneous slug to the undisturbed soil cores. A control treatment received the same depth of deionised water.

The cores were 70 mm in diameter, either 50 or 100 mm deep, and were taken from a Te Kowhai silt loam soil under dairy pasture from the four horizons as described in Table 5.1. The cores were taken from 0-50, 50-150, 300-500, and 500-700 mm soil horizons. In total, 22 soil cores were taken to a depth of 750 mm using a hydraulic soil corer (Giddings and Lewis, Fond du Lac, WI). Further selection of the actual undisturbed cores used for each horizon investigation was necessary to ensure similar soil properties and that no obvious soil discontinuities were present. This subsampling resulted in between 6 and 11 replicates per soil horizon being available for investigation. A PVC plastic pipe was used as a casing to hold the soil cores. Petroleum gel, applied in a molten form, provided a seal between the sides of the soil and the casing, thereby preventing any edge flow effects (Cameron *et al.*, 1992). The casing extended 40 mm above the soil surface to allow the required depth of effluent or water to be applied. A large aperture nylon mesh was used to assist in supporting the base of the cores. The tops of the casings were covered with plastic to prevent any evaporation of the applied effluent or water. Water-only control treatments were used to ascertain the amounts of C leached from native soil organic matter rather than that leached from the applied effluent.

Table 5.1 Description of undisturbed cores used to assess soil filtration parameters.

Horizon depth (mm)	Core height (mm)	Horizon description [†]	Porosity [‡]	Sat. hyd. conduct. [‡] (mm h ⁻¹)	Number soil cores		Description [‡]
					Effluent	Water	
0-50	50	Apg	0.57	11.3	6	5	Dark A horizon dominated by pasture roots
50-150	100	Ap	0.53	119.3	3	3	Dark A horizon with pasture roots
300-500	100	Br1	0.58	3.4	6	3	Silt loam subsoil
500-700	100	Br2	0.58	Dis	5	3	Silt loam subsoil

Dis = Dispersed on saturation

[†] From Clayden and Hewitt, (1989)

[‡] From Singleton, (1997)

Following the effluent application, the cores were flushed twice with two separate 30-mm depth applications of deionised water. Leachates from all three applications were collected separately. Water applications were not started until leachate from the previous application of effluent or water had ceased to drain from the core. The leaching fluid used was deionised water because this had ionic strength (10 $\mu\text{S cm}^{-1}$) similar to that of the local rainwater (4-15 $\mu\text{S cm}^{-1}$). In the field, the greatest amount of leaching of organic material occurs when the soil profile is saturated and rainfall occurs during or shortly after the irrigation event.

The size-class distribution of organic material in each of the leachates was determined in a manner similar to that described for the effluent particle size characterisation. The cleaner leachate from the water-only applications allowed the automated C analyser to be used for all C measurements on these leachates. It was visually evident in all leachates that no material present was greater than 2.0 mm in size, so this filter size was not used.

5.4 Pore size distribution

To help explain the differences observed in the leaching behaviour of different soil horizons, an attempt was made to characterise the size distribution of the soil pores in each horizon. This distribution of cylindrical pores within each horizon was calculated using the relationship (Equation 5.1) derived by Thomasson (1975) and based on the Hagen-Poiseuille capillary rise equation

$$s \leq 2960 / d \quad (5.1)$$

where:

s = applied tension in cm of water

d = equivalent diameter of a cylindrical pore (μm).

Equation 5.1 requires the input of soil moisture release data, which were collected using the method of Klute (1986). Moisture release data for this soil were reported by Singleton (1997) for 2.5, 5, 10, 20, 40, 100 and 1500 kPa tensions using the pressure plate method. The pore diameters associated with the

volume change between two tensions were determined from Equation 5.1. Samples used were from the same site as those used for the particulate filtration experiment.

5.5 Particulate matter transport model

Considering the model on a per unit area basis for a computational time step of dt ,

$$M_i(t) = F_i(t)R_iW_i(t)/U \quad (5.2)$$

$$F_i(t + dt) = F_i(t) - M_{i+1}(t) + M_i(t)(1 - P_i z_i) \quad (5.3)$$

$$T_i(t + dt) = T_i(t) + M_i(t)P_i z_i \quad (5.4)$$

$$P_i z_i \leq 1 \quad (5.5)$$

$$R_i \leq 1 \quad (5.6)$$

where:

M_i = mass of C (g C) transferred to layer i from layer $i - 1$ with the water volume W_i

F_i = free pool (g C) in layer i

T_i = trapped pool (g C) in layer i

W_i = amount of water (mm) transferred to layer i from layer $i - 1$

U = unit flow (mm)

R_i = proportion of the free pool washed out by the unit flow

P_i = proportion of the C mass transferred into layer i that is then trapped per mm of soil.

To simulate the movement of particulate matter applied to soils, it was assumed that the undissolved material can be divided into a number of discrete physical size-classes with varying Carbon:Nitrogen (C:N) ratios. When an effluent is applied to the soil, the model moves the particulate material into the topsoil layer, and a proportion of the material is considered to be “trapped” and is not available for further movement out of the layer, as shown in Figure 5.1. The remaining portion enters the “free” pool in this topsoil layer and may be washed out with further flows. The amount of material that is considered to be “washed out” by a flow event is controlled by the R_i parameter and the size of the water flow. When this “washed out” material enters the next layer it is again split between the trapped and free pools. The proportion entering the trapped pool and the amount moved out of the free pool for a given water flow are parameterised for each soil-class in the effluent and for each soil horizon considered. Material is not considered to be able to move from one size-class to another. The input concentration in a size-class at the soil surface is considered to be reduced with depth as material is removed by filtration.

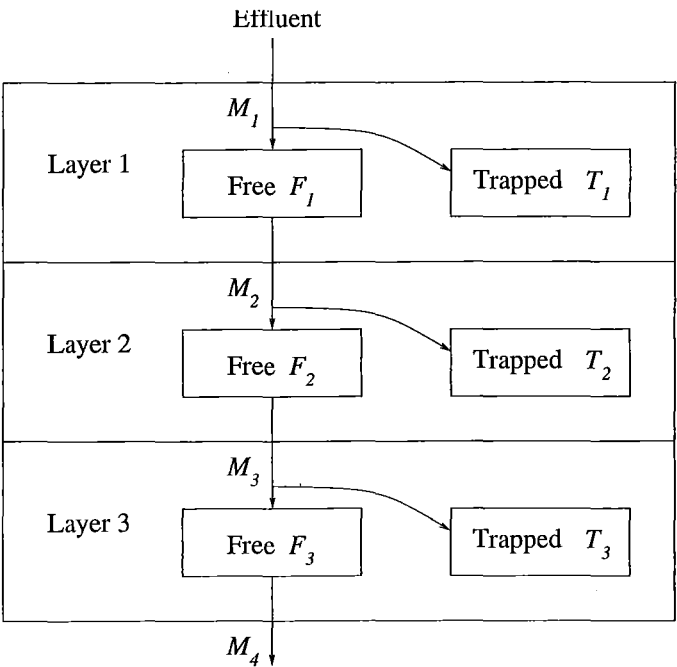


Figure 5.1 Schematic of the model for the movement of particulate material applied to a multilayered soil.

5.6 Parameterisation of the model

The soil water flows between computational zones in the soil cores, caused by effluent or water applications, were modelled with the CSIRO soil water and infiltration model, SWIM (Ross, 1990). The two particulate transport model parameters, R_i and P_i , for each effluent size-class and soil horizon were determined by iterative procedures. This involved matching the predicted mass of C leached to that of the measured values for each size-class and horizon. Bias was shown in the parameter selection process to get the total sum of C leached from all events correct rather than individual masses correct for leaching events.

5.7 Results

5.7.1 Size characterisation of the effluent

The C concentrations were determined on the filtrates produced from the effluent for the various filter sizes ranging from unfiltered down to a 0.2- μm filter. The concentration of C in each size-class (Table 5.2) was determined by taking the difference between the two filtrate concentrations. The two filter sizes used in the calculation determine the physical bounds of the size-class. The percentage that each size-class is of the effluent as a whole is also give in Table 5.2. As explained in the Materials and Methods section, the effluent samples were not filtered sequentially; new raw samples were used for each filter.

Table 5.2 C concentration ($\mu\text{g ml}^{-1}$) for various size-classes for the raw effluent. Also shown is the percentage of the effluent as a whole that each class represents.

	Size-class							
	> 2 mm	2mm to 500 μm	500 to 105 μm	105 to 38 μm	38 to 7 μm	7 to 2.7 μm	2.7 to 0.2 μm	> 0.2 μm
C ($\mu\text{g ml}^{-1}$)	536.5	97.4	64.5	101.8	301.3	335.7	141.4	135.6
Std Error	121	61	69	69	47	45	17	9
As % of total	31.3	5.7	3.8	5.9	17.6	19.6	8.2	7.9

5.8 Application onto undisturbed soil cores

All cores from the Apg (0-50 mm) and Ap (50-150 mm) horizon produced leachate from both the effluent and water control treatments. The subsoils (Br1 and Br2) produced leachate from only two of the six water controls and one of the eleven effluent treatments. As no other replicates produced effluent leachate, the core was not flushed with the two further clean water applications.

The concentrations in the filtrates produced from the various filter sizes for both the leachate from the effluent and the water control treatments are given in Tables 5.3 and 5.4.

Table 5.3 Mean C concentrations ($\mu\text{g ml}^{-1}$) in the filtrates produced from the effluent and water control treatments, as applied to the Apg (0-50 mm) soil cores.

	Filter size						
	Total	500 μm	105 μm	38 μm	7 μm	2.7 μm	0.2 μm
Eff. leachate	680.0	611.6	554.8	435.4	423.4	317.9	98.2
Std Error	77.6	75.2	57.3	48.9	55.5	30.3	7.0
Water control	17.8	18.2	15.5	15.9	13.5	9.1	5.5
Std Error	12.0	11.4	8.4	6.8	8.5	4.4	0.8
1 st H ₂ O leachate	77.8	72.8	77.6	66.3	67.6	58.6	40.0
Std Error	26.7	16.9	17.0	14.8	17.2	12.6	6.5
Water control	13.3	13.3	12.9	12.5	11.9	10.7	9.6
Std Error	3.8	3.3	2.5	2.5	2.8	2.1	3.0
2 nd H ₂ O leachate	50.5	50.6	49.4	45.2	43.2	41.7	39.7
Std Error	7.3	5.7	6.5	6.4	6.6	5.8	5.7
Water control	12.1	12.7	13.1	15.1	11.2	12.4	12.4
Std Error	2.7	3.1	3.3	3.6	2.4	3.0	3.8

Table 5.4 Mean C concentrations ($\mu\text{g ml}^{-1}$) in the filtrates produced from the effluent and water control treatments as applied to the Ap (50-150 mm) soil cores.

	Filter size						
	Total	500 μm	105 μm	38 μm	7 μm	2.7 μm	0.2 μm
Eff. leachate	526	483.6	404.8	342.4	341	339	94.9
Std Error	87.3	104.4	70.2	64.6	55.7	19.8	27.0
Water control	6.5	7.4	7.3	8.1	7.2	8.4	8.0
Std Error	0.3	0.6	0.4	0.3	0.0	0.2	0.3
1 st H ₂ O leachate	88.0	92.9	97.5	87.0	94.0	80.3	47.5
Std Error	20.4	23.6	19.3	18.6	17.3	14.2	8.5
Water control	6.5	7.4	7.3	8.1	7.2	8.4	8.0
Std Error	0.7	1.0	0.2	1.6	1.1	2.5	0.3
2 nd H ₂ O leachate	28.5	31.1	28.2	38.6	28.9	30.3	28.5
Std Error	4.4	7.5	2.1	2.6	1.5	2.3	7.5
Water control	13.4	12.1	12.2	13.9	10.4	9.9	11.4
Std Error	1.0	0.8	1.0	1.5	0.8	1.0	0.6

The mass of C on a size-class basis, leached in each event as a percentage of the total C applied, is given in Tables 5.5, 5.6 and 5.7. The average mass of C in the filtrates produced from the Apg (0-50 mm) horizon from both the effluent and clean water flushes is plotted against filter size in Figure 5.2. The C quantities leached from the water controls have been subtracted from the effluent values so the data represent the effect of effluent application only.

Table 5.5 C in applied effluent and leachates for different size-classes as a percentage of total applied C from the Apg (0-50 mm) cores.

Leachate event	Size-class								Total
	> 2 mm	2mm to 500 μm	500 to 105 μm	105 to 38 μm	38 to 7 μm	7 to 2.7 μm	2.7 to 0.2 μm	> 0.2 μm	
Applied eff.	31.3	5.7	3.8	5.9	17.6	19.6	8.2	7.9	100
Eff. leachate	0.0	3.1	2.4	5.1	0.4	4.5	9.3	3.9	28.7
1 st H ₂ O leachate	0.0	0.4	0.0	0.5	0.0	0.4	0.9	1.4	3.6
2 nd H ₂ O leachate	0.0	0.0	0.1	0.4	0.0	0.1	0.0	1.2	1.8
Total over 3 events	0.0	3.5	2.5	6.0	0.4	5.0	10.2	6.5	34.1

Table 5.6 C in applied effluent and leachates for different size-classes as a percentage of total applied C from the Ap (50-150 mm) cores.

Leachate Event	Size-class								Total
	> 2mm	2mm to 500µm	500 to 105µm	105 to 38µm	38 to 7µm	7 to 2.7µm	2.7 to 0.2µm	> 0.2 µm	
Applied eff.	31.3	5.7	3.8	5.9	17.6	19.6	8.2	7.9	100
Eff. leachate	0.0	1.6	3.3	2.6	0.0	0.3	9.6	3.7	21.1
1 st H ₂ O leachate	0.0	0.0	0.0	0.5	0.0	0.7	1.5	1.8	4.5
2 nd H ₂ O leachate	0.0	0.1	0.1	0.0	0.0	0.4	0.0	0.4	1.0
Total over 3 events	0.0	1.7	3.4	3.1	0.0	1.4	11.1	5.9	26.6

Table 5.7 C in applied effluent and leachates for different size-classes as a percentage of total applied C from the Br2 (600-700 mm) cores.

Leachate Event	Size-class								Total
	> 2mm	2mm to 500µm	500 to 105µm	105 to 38µm	38 to 7µm	7 to 2.7µm	2.7 to 0.2µm	> 0.2 µm	
Applied eff.	31.3	5.7	3.8	5.9	17.6	19.6	8.2	7.9	100
Eff. leachate	0	7.9	5.2	7.3	6.9	18.6	4.4	5.8	56.1

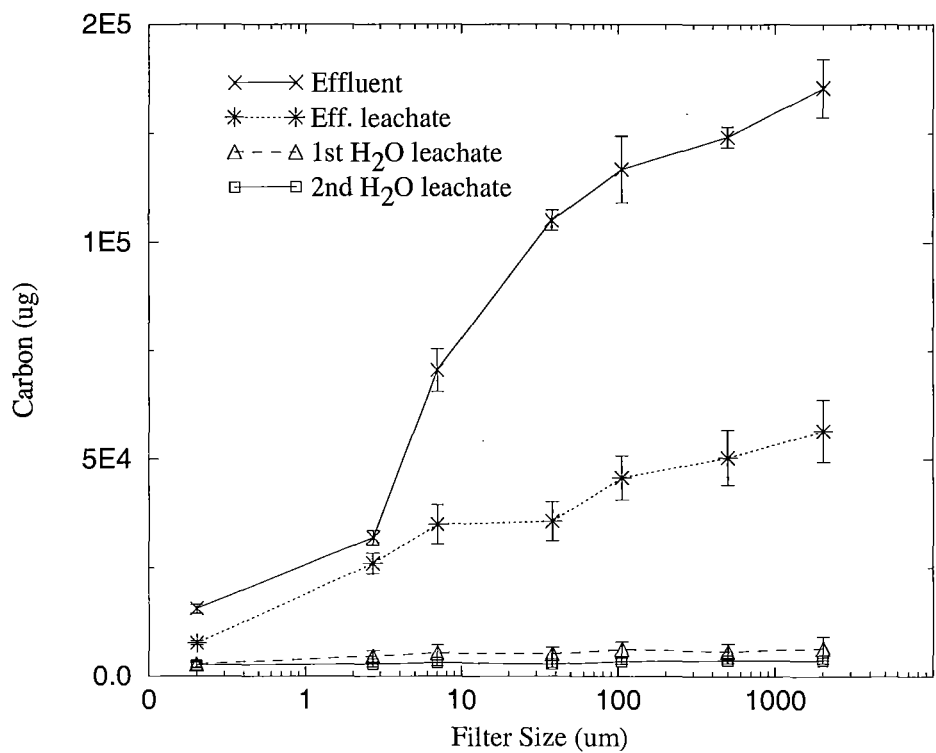


Figure 5.2 Mass of C (µg) in the applied effluent, and in the leachates from the effluent application and the two water flushes for the various filter sizes used, for the Apg (0-50 mm) soil horizon. Water controls have been subtracted.

5.9 Pore size distribution

The pore volume in a size-class, as a percentage of the total pore volume in a horizon, is given in Table 5.8.

Table 5.8 Pore volume in each size-class as a percentage of the total soil pore volume in the Apg (0-50 mm) and Ap (50-150 mm) horizon.

	Size-class							
	Inf. to 120µm	120 to 59µm	59 to 30µm	30 to 15µm	15 to 7µm	7 to 2.9µm	2.9 to 0.2µm	> 0.2µm
Apg (0-50 mm)	3.28	1.76	2.04	5.33	6.57	7.71	22.77	50.50
Std Error	0.37	0.37	0.05	0.69	0.63	0.75	1.97	1.31
Ap (50-150 mm)	4.22	4.98	3.90	5.63	5.79	5.68	10.50	59.4
Std Error	0.95	1.56	0.46	0.32	0.55	1.00	2.32	0.15

5.10 Simulation

The actual C leached per event and the total over the three events are compared with the simulated values in Tables 5.9 and 5.10 for the Apg (0-50 mm) and Ap (50-150 mm) soil horizons.

Table 5.9 Mass of C (µg) leaching, simulated versus actual results for various size-classes for the Apg (0-50 mm) soil cores.

	Size-class						
	2mm to 500µm	500 to 105µm	105 to 38µm	38 to 7µm	7 to 2.7µm	2.7 to 0.2µm	< 0.2µm
Eff. leachate							
actual	6149	4681	9993	817	8872	18303	7702
simulated	6149	4541	9993	768	8872	15741	7702
1 st H ₂ O leachate							
actual	708	0	1066	0	829	1798	2818
simulated	708	187	1066	49	829	1456	2818
2 nd H ₂ O leachate							
actual	0	250	806	0	250	56	2333
simulated	0	0	0	0	0	0	0
Totals							
actual	6857	4931	11865	817	9951	20157	12853
simulated	6857	4541	11059	817	9701	17197	10520
Ratio (act/sim)	1.00	1.09	1.07	1.00	1.03	1.17	1.22

Table 5.10 Mass of C (μg) leaching, simulated versus actual results for various size-classes for the Ap (50-150 mm) soil cores.

		Size-class						
		2 mm to 500 μm	500 to 105 μm	105 to 38 μm	38 to 7 μm	7 to 2.7 μm	2.7 to 0.2 μm	< 0.2 μm
Eff. leachate	actual	3200	6485	5035	0	387	18925	7298
	simulated	2688	5447	5035	0	387	13815	7298
1 st H ₂ O leachate	actual	0	0	1011	0	1432	2896	3611
	simulated	512	1038	1011	0	1432	2572	3611
2 nd H ₂ O leachate	actual	165	216	0	0	817	0	799
	simulated	0	0	0	0	0	0	0
Totals	actual	3365	6701	6046	0	2636	21821	11708
	simulated	3200	6485	6046	0	1819	16392	10909
Ratio (act/sim)		1.05	1.03	1.00	1.00	1.45	1.33	1.07

5.11 Discussion

5.11.1 Effluent size characterisation

More than 30% of the C in the prepared effluent was contained in particles greater than 2 mm in size (Table 5.2), and approximately 90% was particulate, i.e. greater than 0.2 μm in size. This amount of particulate C is higher than other measured values for typical DFE, which were approximately 70% (Macgregor *et al.*, 1979; Barkle *et al.*, 1994). Because the transport of the particulate material was considered on the basis of the fraction applied in a size-class, the impact of a higher than typical value for the total amount of particulate component is considered to be of only minor significance.

The standard errors associated with the C concentrations (Tables 5.3 and 5.4) in the filtrates are a reflection of the differences between the sample replicates. Considering the nonhomogeneous nature of the effluent and leachates, these standard errors are considered acceptable. They are, however, exacerbated when the mass of C is determined on a per size-class basis. This occurs because the size-class calculation involves taking the difference between the means of two filtrate concentrations, and whereas the standard errors become larger, the actual quantity of C becomes smaller. This level of uncertainty in the actual C quantities per size-class needs to be considered when the results from the soil filtration are interpreted. The standard errors in the size-class estimation would have been smaller if sequential sampling methods had been used as this would have allowed a paired analysis of the results. However, this was not feasible because the volume of filtrate from the cellulose filters was too low for sequential sampling.

5.11.2 Soil core leaching results

Both topsoil horizons leached approximately the same amount of effluent-C: 34% for the Apg, and 27% for the Ap horizon (Tables 5.5 and 5.6). This was unexpected because the 100-mm Ap cores were twice the length of the 50-mm Apg cores. However, the hydraulic conductivity is an order of magnitude greater in the Ap horizon (Table 5.1). Also, the distribution of the pore sizes (Table 5.8) indicates that the Apg horizon has nearly twice the porosity in the larger pore size-class, i.e. > 30 μm pore diameter compared with the Ap horizon. It is possible that the greater pore volume in the larger size allows more particulate movement per mm of soil thickness.

The result could also indicate the existence of continuous macropores, or root channels, that allow for bypass flow. Leachate quality produced from these pores would be independent of the length of the core. It should be recalled, however, that the cores were preselected to ensure that visually large (i.e. > approximately 2 mm) holes or discontinuities were not present in the faces of the cores. This preselection process did not discount the existence of pores smaller than this size, which may still contribute to bypass flow, or pores that were not visible in the surface faces of the cores. The pore size at which bypass flow ceases to be an important phenomenon is not known.

Most of the effluent-C leached from the topsoil cores (Apg and Ap) occurred in the initial drainage event from the application of the effluent. The cores were pre-wetted and at field capacity so this result was not unexpected. The 30-mm applied depth approximates the pore volume of the Apg (0-50 mm) topsoil core and is about half that of the Ap (50-150 mm) core. In both horizons, the C quantity in this initial leachate represented approximately 82% of the total C that was leached. In the final water-only flush, the C content in the leachate had dropped to approximately 5% of the total quantity leached.

Only two of six water controls for the subsoils (Br1 and Br2) produced leachate. It is suspected that this was caused by the dispersive nature of the soil, i.e. when it is sampled and then saturated it expands and blocks up the pore space. This behaviour was reported by Singleton (1997) when the saturated hydraulic conductivity data were obtained for the Br2 soil horizon.

Only one of the eleven subsoil cores produced leachate from the effluent application. This core drained very rapidly compared with the other cores, and the leachate contained 56% (Table 5.7) of the C from the applied effluent. This core was reinspected visually, and a macropore hole was evident in the bottom face of the core, which may have accounted for the rapid bypass flow behaviour.

As can be seen in Figure 5.2, the majority of the C material removed or filtered out by the Apg (0-50 mm) topsoil horizons originated in the larger size-classes. The C in the leachates from the water-only flushes is dominated by the smaller size fractions. The smallest size-class, which is the dissolved C fraction, was still showing significant amounts of C in the final leachate. For the Apg (0-50 mm) horizon, this third leaching event had 18% (1.2 of 6.5%, Table 5.5) of the total amount of C that was leached in this class, whereas the Ap horizon had 7% (0.4 of 5.9%, Table 5.6).

The actual C concentrations in the leachates draining from the water-only control cores were low compared with those from the effluent cores and were dominated by the dissolved fraction of C. The mean

C concentrations from all three water applications from the Apg (0-50 mm) cores were higher at 14.4 ppm than the 8.8 ppm from the Ap (50-150 mm) soil horizon (Tables 5.3 and 5.4).

In both topsoils, the second smallest size-class, 2.7-0.2 μm , seemed to show more material leached from the effluent soils cores than was actually applied in the effluent. One possible explanation for this is that C material from the larger size-classes may have physically broken down as it passed through the soil core. This would have allowed material to transfer into the smaller size-classes and increases the apparent leached component in this range. Another possible explanation is that when the larger size-class materials were measured in the effluent, they had smaller particles attached or bound to them. When passing through the soil core, this smaller material became unbound and increased the apparent leachate from the small size-class.

Elevated output, compared with input, was not seen in the smallest class ($< 0.2 \mu\text{m}$). Material in this size range is adsorbed to the soil surface (Liang *et al.*, 1996; Brown and Barkle, 1996). This behaviour has been modelled by both the Freundlich (Brown and Barkle, 1996) and Langmuir equations (Liang *et al.*, 1996). If the adsorption of the dissolved fraction by the soil was high enough, then even with additional material entering the class, the leached component would not have exceeded the amount applied.

The other size-class that seemed to exhibit abnormally high leaching characteristics in both horizons was the 105-38 μm size. In this instance, the large uncertainties associated with the amount of C actually applied in the effluent (Table 5.2) in that particular size-class (105-38 μm) and in the size-class above it (500-150 μm) could have led to this result. Each of these two size-classes was relatively small and contributed only 5.9 and 3.8% respectively, of the total C in the applied effluent.

5.11.3 Pore size distribution

The pore size distribution data (Table 5.8), provided good evidence, as discussed earlier, for greater leaching behaviour in the Ap horizon than in the Apg horizon. The distribution information alone, however, could not predict the non-leaching behaviour of the subsoils (Br1 and Br2). It was the dispersive nature of the subsoils under the experimental conditions that dominated the non-leaching results.

Although the pore size distribution was a good indicator of particulate behaviour when applied to the two topsoils, without similar trials on a much wider range of soils, the usefulness of this index can not be ascertained. The shape of the pore sizes could also be an important factor. It was assumed in the capillary equation (Equation 5.1) that the pores were cylindrical in shape and this may not be valid for certain soils. Further work of a similar nature is planned over a wider range of soil types to explore fully the concept of being able to use pore size distribution data to assist in parameterising the particulate model.

5.11.4 Simulation

The simulated response for the total amount of C leached over the three events closely approximated the observed values (Tables 5.9 and 5.10) for both soils horizons. The two parameters “trapped” and “washed” were fitted. The exceptionally good fit, in cases where the C was leached only in the first and/or second leaching events, shows that the model prediction with two parameters can be fitted accurately to the measured data. The exceptions are when the amount of leached material measured from a particular size-class was greater than that measured in the applied effluent. This occurred for the 2.7-0.2 μm size-class in both horizons and for the 105-38 μm size-class in the Ap horizon. Inasmuch as the proposed transport model does not consider that material can be moved from one size-class to another, it is unreasonable to expect the model to be able to predict this behaviour.

The model was very good at predicting the distribution of C within the two initial leaching events. It was not possible to fit parameters that showed the low level of C leaching observed in the final water flush (Tables 5.9 and 5.10). Any parameters that gave non-zero predictions for the final flush gave unacceptable results for the first two events (data not shown), in which 95% of the C leaching occurred. This may reflect either a continuum of states between the simple “trapped” and “free” pools employed by this model or processes that are not adequately described by the model, such as transfer of material between classes.

The simulated distribution of the effluent-C for the Apg soil horizon 30 and 60 min into an effluent application event is shown in Figure 5.3. Particulate matter seems to have the potential to penetrate to depth in the more porous upper layers of this soil. Such infiltration has significant implications in terms of effluent decay dynamics, as this particulate matter is believed to become available to microbial populations with time and so may influence the vertical distribution of those populations.

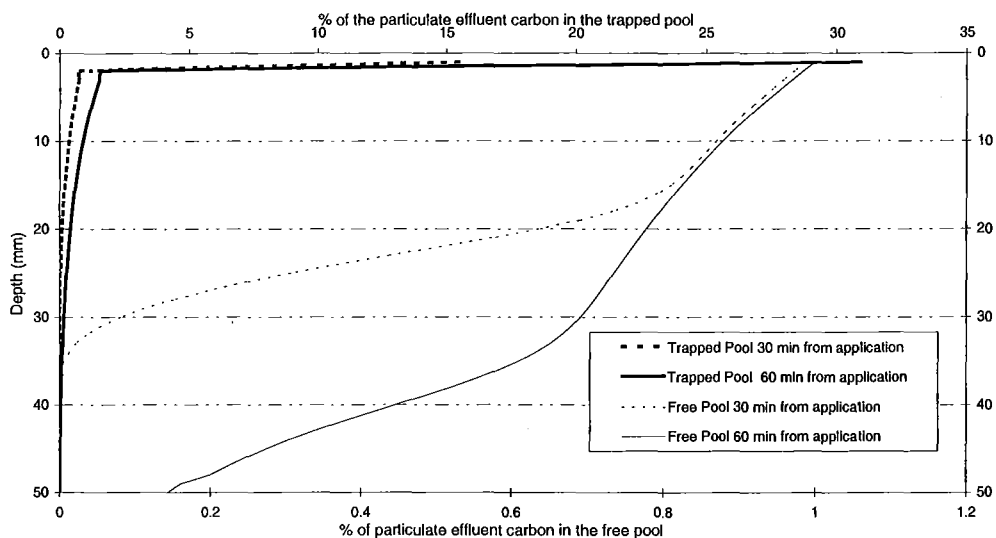


Figure 5.3 Simulated particulate effluent-C movement in the Apg (0-50 mm) horizon 30 and 60 min from the start of the application of the effluent. “Trapped” and “free” pools are shown on different X axes as a percentage of the applied particulate effluent-C.

5.12 Conclusions

For the top horizons of the silty loam Te Kowhai soil investigated, significant particulate organic matter can be leached from an effluent application when the soil has a high moisture content. Most of this leaching occurs in the initial application onto the soil.

The potential for particulate organic matter to move into some soils under certain conditions needs to be recognised when effluent treatment sites are being designed and monitored for sustainable operation.

A model was proposed that described the particulate movement of effluent material in terms of filtering and trapping within a soil horizon and then subsequent washing out with flow events. This model was successfully parameterised for the two topsoil horizons considered and, as such, was capable of modelling the movement of particulate materials from effluent applied onto soils.

5.13 References

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Chapter Six

The adsorption kinetics of ammonium and dissolved organic fractions of DFE added to soil

The objectives of this Chapter are to:

Develop an equation that describes the non-equilibrium adsorption kinetics of ammonium and dissolved organic fractions of DFE added to soil

Undertake laboratory experiments to measure the adsorption kinetics of these materials

Parameterise the adsorption equations based on the experimental results

6.1 Introduction

The application of organic effluents onto land is an attractive treatment option, as potentially many of the nutrients in the effluent can be recycled through plant uptake. The efficiency of the treatment relies on the ability of the soil-plant system to filter suspended solids and adsorb dissolved compounds onto soil and root surfaces. Nutrients that are adsorbed onto root surfaces may be taken up by the plant if they are in a suitable form. Molecules that have been adsorbed onto soil surfaces must firstly be desorbed into the soil solution form before they are available for plant uptake, microbial mediation or leaching. The relationship between the amount of a substance adsorbed and the concentration in solution is known as the adsorption isotherm (Jury *et al.*, 1991).

DFE is a very dilute organic mixture of faeces and urine formed from the cleaning operation of the milking parlor and associated holding yards. The total solids content of the effluent is generally less than 1% (Longhurst *et al.*, 2000) and typically 60-85% of the total N present is in an organic form. Of this organic N fraction 20-45% is in a dissolved form (Barkle *et al.*, 1999), with approximately 30% of the C also being dissolved (Barkle *et al.*, 1994). The most important components in the adsorption dynamics of DFE are ammonium N ($\text{NH}_4\text{-N}$), nitrate N ($\text{NO}_3\text{-N}$), and dissolved organic matter (DOM).

The adsorption of a molecule involves both chemical and physical interactions between the soil and the molecule in the dissolved phase. Mortland (1970) and Theng (1974) report that electrostatic, ion-dipole interaction, coordination to adsorbed metal ions, hydrogen bonding and Van der Waals interactions may all be important in clay-organic interactions. Riffaldi *et al.* (1998), reviewing adsorption of dissolved organic carbon (DOC) from farmyard manure onto soil, report that solution pH, amorphous Fe and Al oxides, organic matter and clay minerals are important control factors in DOC adsorption. Jardine *et al.* (1989) and Baham and Sposito (1994) found that physical adsorption driven by favourable entropy changes and secondary ion exchange were the predominant mechanisms affecting DOC adsorption in the soil.

Soil particles normally carry a negative charge responsible for the cation exchange properties of the soil. While the ammonium fraction of DFE is positively charged, the net charge of the dissolved proteinous material is unknown. Russell (1982) reports that the protein derived from meat slaughterhouse effluent is negatively charged at neutral pH and therefore little adsorption of proteins would be expected.

In this Chapter the isotherm equations used to simulate the non-equilibrium adsorption kinetics of the NH_4 and DOM implemented in CaNS-Eff are developed, and the laboratory experiments undertaken to parameterise these equations are described.

6.2 Isotherm kinetics

The shape of the isotherm relationship depends on the characteristics of the adsorbent and adsorbing surface and often the other constituents in solution. There are two common types of isotherms: Langmuir and Freundlich.

The Langmuir isotherm (Langmuir, 1918) is described by:

$$C_a = \frac{a Q C_l}{1 + a C_l} \quad (6.1)$$

where:

C_l = solution concentration

C_a = number of adsorbed molecules per unit mass of surface

Q = number of adsorption sites per unit mass

a = rate constant.

The Freundlich isotherm is described by Jury *et al.* (1991) as:

$$C_a = K_f C_l^{1/N} \quad (6.2)$$

where:

K_f and N = constants.

The Langmuir isotherm assumes that at equilibrium the rate of adsorption (r_a) must equal the rate of desorption (r_d). The rate of desorption will be proportional to the number of adsorbed molecules per unit mass of surface (C_a). Hence at equilibrium:

$$r_d = k_1 C_a \quad (6.3)$$

where:

r_d = rate of desorption

k_1 = rate constant for desorption.

The rate of adsorption is proportional to the concentration in solution and also to the number of unfilled sites on a surface, which can mathematically be described by:

$$r_a = k_2 C_l (Q - C_a) \quad (6.4)$$

At equilibrium $r_a = r_d$, equating (6.3) and (6.4) results in:

$$k_1 C_a = k_2 (Q - C_a) C_l \quad (6.5)$$

and solving for C_a results in Equation (6.1) where the constant $a = k_2/k_1$.

It seems likely that equilibrium is reached within two hours for simple molecules (Johnson and Farmer, 1993), so that the lack of a time component in Equations (6.1) and (6.2) is not unreasonable. However, proteins and other complex compounds may take up to 20 hours to reach equilibrium (Russell, 1982). For irrigation and infiltration of DFE into the soil it is apparent that the rate of adsorption at smaller time scales, e.g. 15 minutes, becomes important. In a non-equilibrium situation such as this, instead of assuming that equilibrium conditions exist ($r_a = r_d$), the transient adsorption state can be derived by

describing the change in the adsorbed component as the difference between adsorption (6.4) and desorption (6.3) equations which can be written as

$$\frac{dC_a}{dt} = k_2 (Q - C_a) C_l - k_1 C_a \tag{6.6}$$

where:

k_1 = desorption rate constant

k_2 = adsorption rate constant.

Equation (6.6) is the non-equilibrium isotherm equation implemented in CaNS-Eff, excepting the amount adsorbed and the maximum adsorption amounts are described in terms of per g of soil instead of number of adsorption sites per surface area, with the rate constants adjusted accordingly.

6.3 Parameterisation

Within the CaNS-Eff model there are four classes which are considered to be dissolved:

- NO_3 Nitrate nitrogen
- NH_4 Ammonium nitrogen
- DOMhighCN Dissolved organic matter, high C:N ratio
- DOMlowCN Dissolved organic matter, low C:N ratio.

As nitrate adsorption onto soil is considered negligible in most cases, nitrate is simulated in only the dissolved phase. The adsorption kinetics of DOMhighCN and DOMlowCN are assumed to be identical. To determine the three parameters (Q , k_1 , k_2) for ammonium and DOM, batch trials following the procedure of Johnson and Farmer (1993) were undertaken.

6.4 Method

Samples from four soil horizons of Te Kowhai soil were used in the batch experiment (Table 6.1).

Table 6.1 Soil horizons for Te Kowhai soil used in batch trials to determine adsorption kinetic parameters.

Horizon	Horizon depth (m)	% Clay	Horizon name ^A
1	0.0 - 0.10	38	Apg
2	0.10 - 0.25	40	Ap
3	0.25 - 0.35	39	BgC
4	0.35 - 0.60	30	Br

^A See Clayden and Hewitt, 1989

Grass and litter were cut away from the soil surface. Samples were then passed through a 5 mm sieve and root material removed. Subsequently, the soils were allowed to air dry. DFE was collected from Number 1 Dairy, Dairying Research Corporation, Ruakura, and filtered through flushed 0.2-µm Sartorius AG cellulose acetate filters to provide a “dissolved-only” fraction of DFE. Thirty mls of effluent at concentrations shown in Table 6.2 were shaken on ice with 6 g of air-dried soil from each of the horizons, for 300 seconds or 7200 seconds. After this time the effluent-soil mixtures were filtered through the 0.2-µm filters. Samples were analysed for NH₄-N using standard auto-analyser techniques (Blakemore *et al.*, 1987). DOC was measured to represent the DOM as used in CaNS-Eff. The DOC was measured using an automated C analyser (Shimadzu, TOC 5000) which uses combustion followed by non-dispersive infra-red detection of CO₂ gas.

Table 6.2 Dilution series for DFE used for adsorption batch trials.

Concentration factor	NH ₄ -N (µg g ⁻¹)	DOC (µg g ⁻¹)
0.05	6	16
0.25	25	62
0.50	56	138
1.00	96	360

6.5 Results

The NH₄-N concentrations in each dilution series and in the soil solution after 300 and 7200 seconds for each of the four soil horizons are given in Table 6.3. The corresponding data for DOC are given in Table 6.4.

Table 6.3 NH₄-N concentrations in the DFE solution and in shaken soil solutions after 300 and 7200 seconds for each of the four soil horizons.

NH ₄ -N concentration in DFE solution (mg l ⁻¹)	NH ₄ -N concentration in solution (mg l ⁻¹)							
	Horizon 1		Horizon 2		Horizon 3		Horizon 4	
	300 s	7200 s	300 s	7200 s	300 s	7200 s	300 s	7200 s
0	0.4	0.5	0	0	0	0.2	0	0
6	3.2	3.2	2.0	1.7	1.3	1.0	1.2	1.0
25	15	13	12	11	8.1	9.0	28	26
56	34	26	28	28	24	22	26	24
96	60	60	64	56	56	56	68	60

Table 6.4 DOC concentrations in DFE and in shaken soil solution after 300 and 7200 seconds for each of the four soil horizons.

DOC concentration in DFE solution (mg l ⁻¹)	DOC concentration in solution (mg l ⁻¹)							
	Horizon 1		Horizon 2		Horizon 3		Horizon 4	
	300 s	7200 s	300 s	7200 s	300 s	7200 s	300 s	7200 s
16	4.5	10.5	10.5	6.8	3.2	0	1.3	1.7
62	38.1	79.2	79.2	62.1	72.4	35.0	42.5	69.2
138	102.1	110.5	110.5	115.3	109.8	72.0	82.2	101.0
360	318.9	315.1	331.3	306.8	296.2	268.2	278.1	259.4

6.6 Analysis

The maximum amount of NH₄-N or DOC (Table 6.5) that can be adsorbed per g of soil was estimated from the fitted trend curve of the adsorbed material versus the total material in the system for each soil horizon. For example, Figure 6.1 for NH₄-N and Figure 6.2 for DOC.

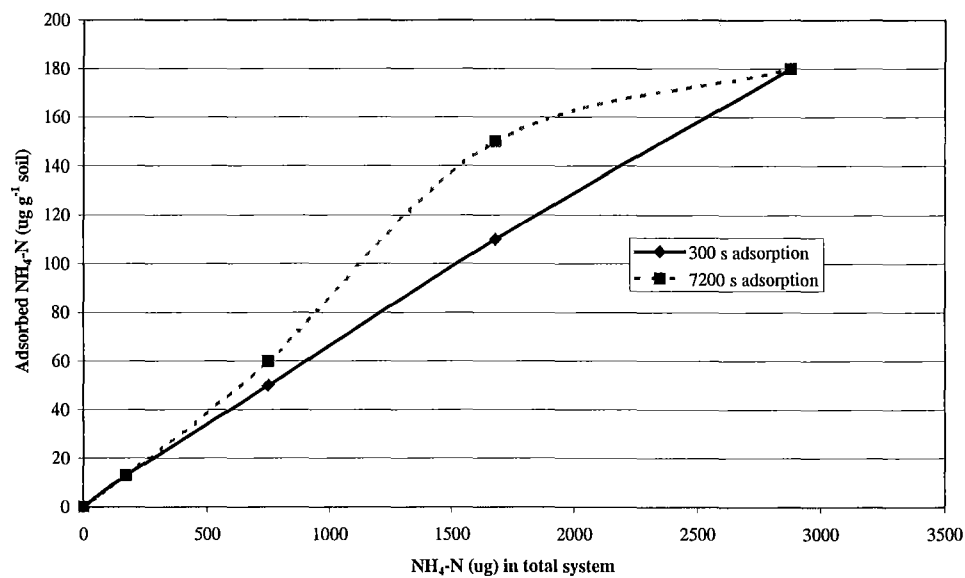


Figure 6.1 NH₄-N adsorption versus NH₄-N in the total system for Horizon 2 of Te Kowhai soil.

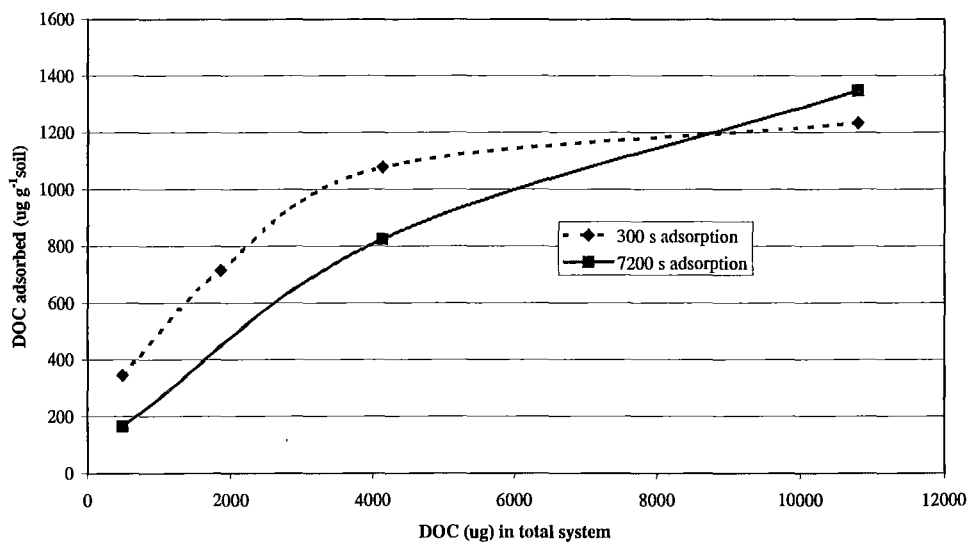


Figure 6.2 DOC adsorption versus DOC in the total system for Horizon 1 of Te Kowhai soil.

Table 6.5 Maximum adsorption capacity (g N or g C g⁻¹ soil) of NH₄-N and DOC for each of the four soil horizons.

Horizon	Maximum adsorption capacity (g N or g C g ⁻¹ soil)	
	NH ₄ -N	DOC
1	2.0E-4	2.4E-4
2	2.1E-4	3.5E-4
3	2.0E-4	5.5E-4
4	2.8E-4	6.5E-4

As no analytical method was available to determine the desorption and adsorption constants (k_1 and k_2), software was developed that allowed for visual calibration. The ten adsorption data points, five for 300 seconds and five for 7200 seconds, were simultaneously displayed. By concurrently fitting curves to both the 300 and 7200 second data (Figures 6.3 and 6.4), the desorption and adsorption constants for each horizon species were determined (Table 6.6).

Table 6.6 Desorption (k_1) and adsorption (k_2) constants for $\text{NH}_4\text{-N}$ and DOC derived for each of the four soil horizons.

Horizon	Desorption and adsorption constants			
	$\text{NH}_4\text{-N}$		DOC	
	$k_1 \text{ (s}^{-1}\text{)}$	$k_2 \text{ (s}^{-1}\text{)}$	$k_1 \text{ (s}^{-1}\text{)}$	$k_2 \text{ (s}^{-1}\text{)}$
1	6.8E-4	84.35	3.38E-3	58.22
2	1.23E-3	121.82	1.19E-3	10.29
3	5.13E-4	153.06	4.74E-4	9.03
4	1.52E-3	250.00	2.25E-3	17.53

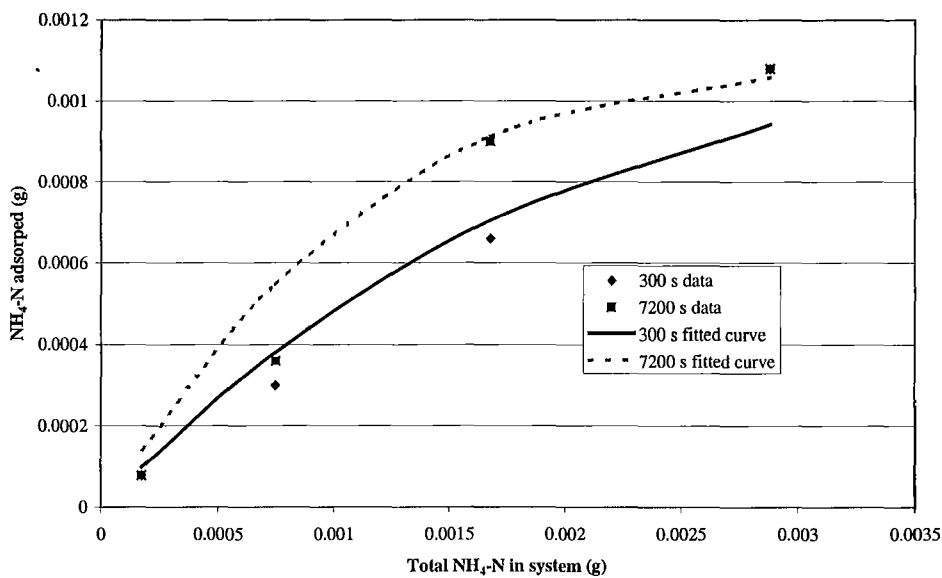


Figure 6.3 Fitted isotherm curves for $\text{NH}_4\text{-N}$ for Horizon 1 soil after 300 and 7200 seconds.

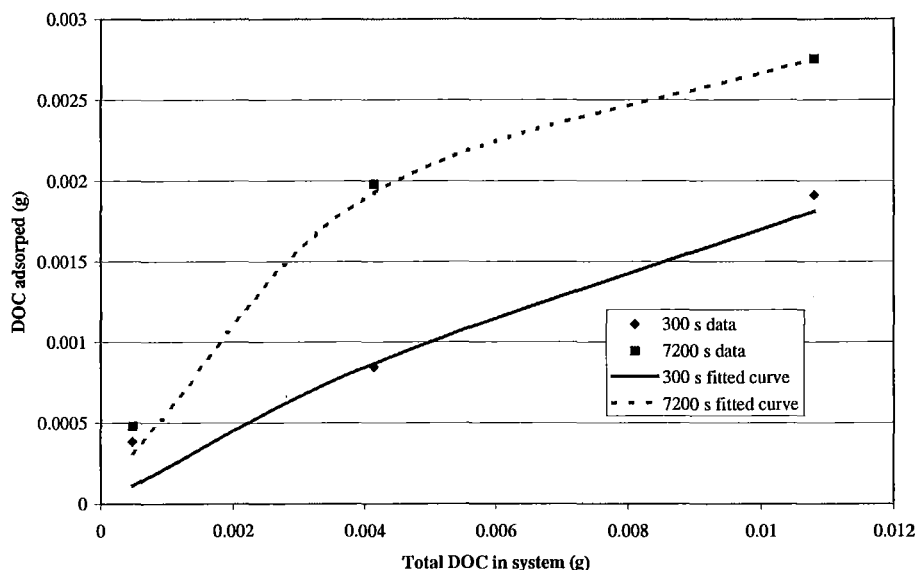


Figure 6.4 Fitted isotherm curves for DOC for Horizon 3 soil after 300 and 7200 seconds.

6.7 Isotherm behaviour

The transient behaviour of the adsorbed and dissolved NH_4 under batch trial conditions (6 g soil, 30 ml water) for a slug addition of $1.68\text{E-}3$ g (56 ppm) of $\text{NH}_4\text{-N}$, assuming no N transformations, is shown in Figure 6.5. This result indicates that under these conditions equilibrium between adsorbed and dissolved $\text{NH}_4\text{-N}$ would be obtained after approximately 1100 seconds (18 minutes). At this time approximately $9.0\text{E-}4$ g of $\text{NH}_4\text{-N}$ would be adsorbed, which represented 75% of the potential adsorption sites being filled.

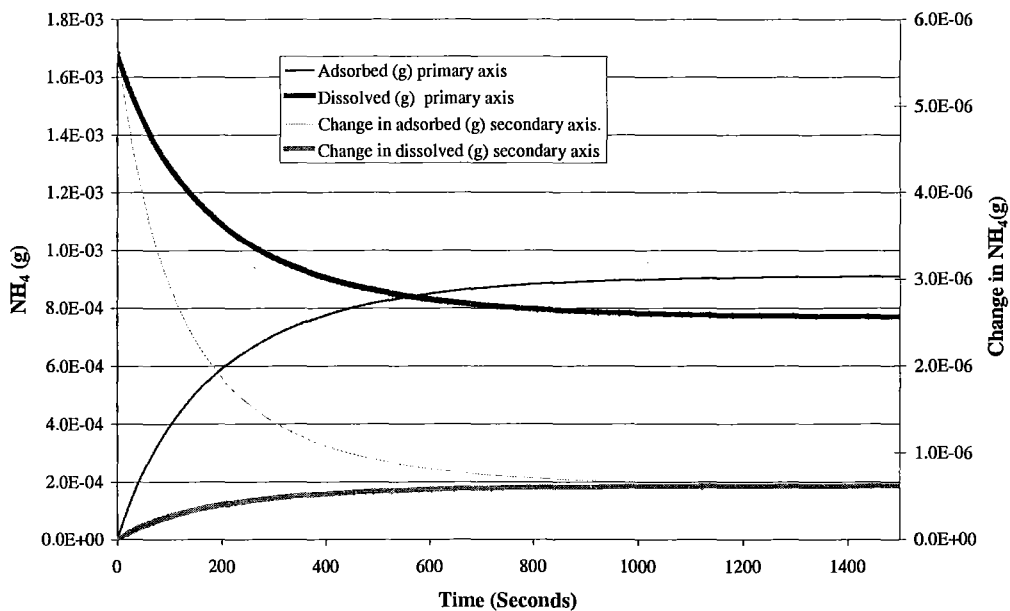


Figure 6.5 Transient behaviour for adsorption and dissolved $\text{NH}_4\text{-N}$ following a slug addition of $1.68\text{E-}3$ g of $\text{NH}_4\text{-N}$ to 6 g of Horizon 1 soil in 30 ml water with no N transformations.

Under the same simulation conditions, except adding $4.14\text{E-}3$ g of DOC (138 ppm) to Horizon 3 of Te Kowhai soil, the transient adsorption and dissolved behaviour of DOC is given in Figure 6.6. Equilibrium conditions took longer to establish and were only reached after 2500 seconds (45 minutes) when $1.9\text{E-}3$ g of DOC was adsorbed, which represented 57% of the adsorption sites being occupied.

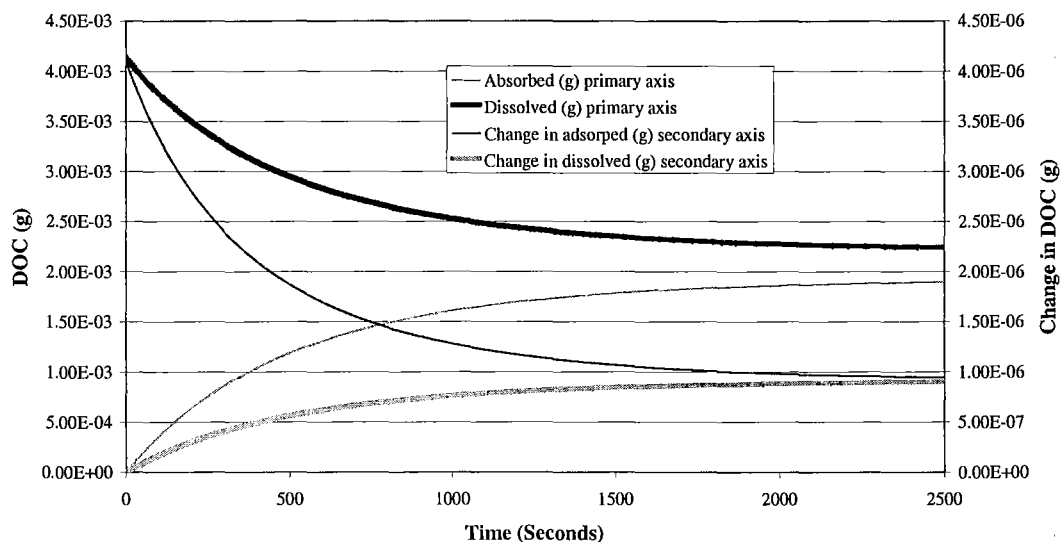


Figure 6.6 Transient behaviour for adsorbed and dissolved DOC following a slug addition of $4.14\text{E-}3$ g of DOC to 6 g of Horizon 3 soil in 30 ml water with no DOC transformations.

6.8 Conclusions

The non-equilibrium form of the Langmuir equation implemented in CaNS-Eff (Equation 6.6) requires more parameters than other frequently used equations. It is however a function of time, and is able to represent low and high concentration conditions. Both these attributes are required for the adsorption kinetics in CaNS-Eff where rapid infiltration of DFE and highly variable soil moistures occur.

The parameterised non-equilibrium isotherm equations for $\text{NH}_4\text{-N}$ and DOC, as determined in this Chapter, were used in the CaNS-Eff model with the following assumptions and adjustments. The DOC adsorption characteristics as measured represent the DOMhighCN and DOMlowCN class in CaNS-Eff. The maximum DOC adsorption amount determined in the batch experiment was reduced by 50% and used for the DOMhighCN and DOMlowCN, as it was considered they could both adsorb to the same sites. As shaken batch trials measure all potentially available soil adsorption sites, of which a large fraction may not be actually available under intact field conditions, the maximum NH_4 adsorption amount was reduced to 33% of that determined. This reduction was not applied to the DOMhighCN and DOMlowCN parameters, as organic molecules can be considered to “self-adsorb” onto organic material already adsorbed. As adsorption is considered to occur in both the micropore and mesopore domains, the maximum adsorption amounts measured were split between the micropore and mesopore domains on the basis of the percentage of water in each domain at saturation.

6.9 References

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Chapter Seven

Impact of controlled drainage on N leaching and solute behaviour

The objectives of this Chapter are to:

Report the leaching and pasture uptake data from the third year of DFE irrigated onto controlled drainage lysimeters, which provides a data set for testing the CaNS-Eff model

Investigate the effect of controlled drainage on nitrate leaching from DFE and DFE amended with nitrate

Use a conservative tracer to determine the bypass flow characteristics from DFE irrigation events and the effect that controlled drainage, application rate and irrigation history have on bypass flow

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7.1 Introduction

In New Zealand regulatory authorities have promoted the use of land-based waste treatment systems as the best practical option for the effective treatment of effluents. However, under certain conditions the ability of some New Zealand soil types to effectively assimilate the N from these applied effluents has been questioned (Selvarajah, 1996). If land-based treatment systems are not designed and operated on sound scientific and engineering principles, contamination through leaching of unused or untreated nutrients to the receiving water can occur. New Zealand already has elevated groundwater nitrate levels in several shallow aquifer systems. In two large districts, Waikato (Selvarajah *et al.*, 1994) and the Waimea Plains (Rosen, 1997), over half of the shallow bores already have nitrate-N concentrations exceeding the 11.3 mg l⁻¹ NO₃-N New Zealand drinking water standard.

One of the major producers of effluent in New Zealand is dairy farming. With over 14,500 dairy farms and 2.8 million cows (LIC, 1995) the effluent produced from cleaning the milking parlours alone is approximately equivalent (based on biological oxygen demand) to the human population of New Zealand. Traditionally, dairy farms have been located on poorly drained soils which have high water holding capacities. These poorly drained soils provide an excellent opportunity to enhance waste treatment processes by manipulating the soil water content to enhance biological denitrification through controlled drainage (Gilliam *et al.*, 1979; Gilliam and Skaggs, 1985; Evans *et al.*, 1991). In response to this opportunity a three-year lysimeter study involving the application of dairy farm effluent (DFE) onto poorly drained soils was initiated. The soil type was a Te Kowhai silt loam with three drainage treatments being investigated; a conventionally drained soil profile and two levels of controlled drainage. The development of the lysimeter facility and early results have been reported previously (Barkle *et al.*, 1994; Barkle *et al.*, 1995; Singleton *et al.*, 2001).

In this Chapter, the focus is on the results from the third year of operation, where the treatment loadings were expanded to include a nitrified effluent in addition to the DFE and water-only control. Bromide tracer experiments were also undertaken to help explain the N leaching results.

7.2 Methods and materials

As details of the construction and operation of the lysimeter facility have been reported elsewhere only a brief summary of these follows. Twelve undisturbed soil lysimeters (0.6 m dia. by 1.2 m deep) were collected using the method of Cameron *et al.* (1992). A petroleum jelly sealant was used to prevent water and/or effluent preferentially draining between the soil core and the lysimeter casing. The lysimeters were installed at ground level as shown in Figure 7.1 to avoid undesirable temperature effects on the microbial assimilation processes.

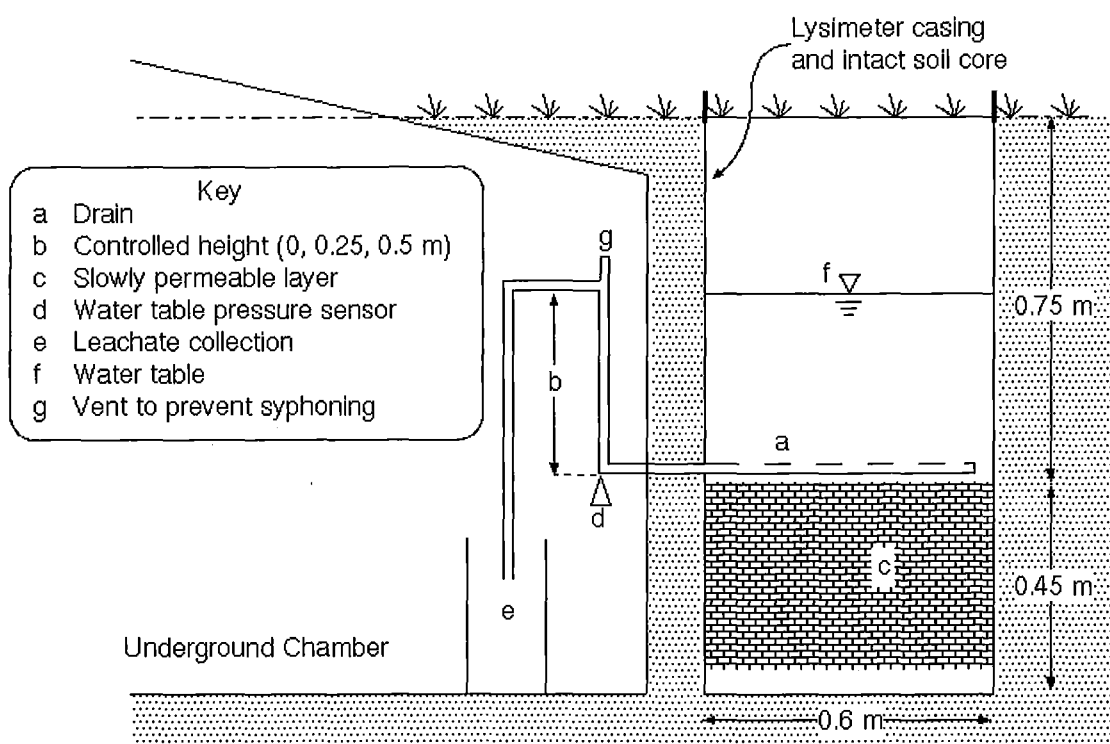


Figure 7.1 Schematic of lysimeter site layout.

The Te Kowhai silt loam is classified as a Typic Orthic Gley (Hewitt, 1992) or a Typic Ochraqualf (Soil Survey Staff, 1990). A brief summary of relevant soil properties by horizon is presented in Table 7.1. Wormholes and interpedal partings have been found to extend to depths greater than 0.6 m in this soil (Singleton *et al.*, 2001).

Table 7.1 Relevant soil properties for Te Kowhai soil (Singleton, 1997).

Horizon	Approx. depth range (cm)	Texture	Clay %	Saturated hydraulic conductivity (mm h ⁻¹)
Apg	0-5	Silt loam	38	11.3
Ap	5-20	Silt loam	40	119.3
Bgc	20-30	Silt loam	39	510.5
Br1	30-50	Silt loam	30	3.4
Br2	50-70	Silt loam	29	Dispersed
2Bg	70-80	Silty clay	55	0.1
2Brx	80-100	Silty clay	60	0.01
3Cr	100-110	Fine sand	7	0.00
4Cr	110-120+	Med. Sand	7	315.6

In the field, water perches on the very slowly permeable layer at about 0.75 m for several months of the year (Singleton, 1991). This perching behaviour makes the soil ideal for investigating the potential benefits of manipulating soil water content. Drainage outlet tubes were installed on the perching layer, at approximately 0.75 m from the soil surface. Three drainage treatments were imposed as shown in Table

7.2. Each drainage treatment was replicated four times; three replicates received effluent application while the fourth was a water-only control.

Table 7.2 Drainage treatments imposed on the lysimeters.

Drainage treatment	Height of weir	Depth to water table
Conventional drainage	No weir	75 cm
Controlled drainage-low	25 cm	50 cm
Controlled drainage-high	50 cm	25 cm

DFE is a very dilute organic slurry produced from the wash-down of the milking parlour and associated holding yards. It was applied to the lysimeters on a weekly basis during the milking season from August 1994 to May 1995. Leachate and pasture data is based on a 12-month period from August 1994 to September 1995, which includes four months after the last effluent application.

The leachate results for the first two years of operation of the lysimeters (Singleton *et al.*, 2001) showed very little nitrate-N being leached. Consequently an additional treatment, which included nitrate in the applied effluent, was imposed at the start of November 1994. This was done by adding sodium nitrate to the DFE and then applying this nitrified effluent (nitrified-DFE) to a set of drainage lysimeters.

All effluent or water irrigations applied onto the lysimeters were of a 17 mm depth over 3.5 hours. This application rate, of 4.9 mm h⁻¹, was chosen to try and avoid surface ponding and minimise preferential flow. The rate used was based on the measured unsaturated hydraulic conductivity data for the topsoil. The irrigations were controlled using a fast-acting solenoid valve coupled to a rose-head sprinkler. The sprinkler and valve assembly was then fitted beneath a bucket placed on a frame above each lysimeter. The measured quantity of water or effluent was then irrigated from the bucket. The valve was programmed to be on for 3 seconds and then off for 2 minutes, simulating the operation of a sprinkler irrigation system as is commonly used for effluent application.

The leachate from the lysimeters was generally collected on a daily basis, with boric acid used as a preservative. The samples were stored at 1°C, volumetrically bulked and analysed on a weekly basis for N and C components. The pasture, a ryegrass-clover (*Lolium perenne* L. / *Trifolium repens* L.) mix, was grown on all lysimeters under a “cut and carry” regime where the pasture was cut and removed every 28 days. On the water-only treatments, 50% of the cut pasture was returned to ensure adequate nutrient supply for pasture survival.

7.2.1 Bromide tracer experiments

The first bromide tracer experiment was conducted in August 1995, three months after the last effluent application. By this time the lysimeters had received DFE for three milking seasons. The bromide was added as a potassium bromide solution in an irrigation event onto all lysimeters. The soil cores at this time were fully wet and water tables were present in all controlled drainage treatments. The initial leachate from this irrigation was collected and analysed after every 500 ml (1.8 mm) of drainage until drainage

ceased approximately 24 hours after the initiation of irrigation. Following this initial collection, leachate generated by rainfall and/or supplementary irrigation was collected daily until approximately two-pore volumes had been recovered. Bromide concentration in the leachate was analysed with a UNICAM™ bromide selective electrode, calibrated every time measurements were made.

A second set of bromide tracer experiments was run 14 months later in October 1996. The cores at this time were pre-irrigated to ensure that they were fully wet and water tables were present as in the previous investigation. This work was done to see if the absence of regular DFE applications had influenced the amount of bypass flow that would occur in an irrigation event. Two application rates were used to investigate the influence of the irrigation rate on the amount of bromide recovered from the irrigation event.

7.3 Results

7.3.1 Effluent loading

In total, 40 effluent applications were made over the milking season resulting in a total N loading of 1554 kg N ha⁻¹ on the DFE treatments. With the additional 243 kg N ha⁻¹ of nitrate-N being added to the nitrified-DFE, the total N loading on this treatment was increased to 1797 kg N ha⁻¹. The effluent loading rates by N components are shown in Table 7.3.

Table 7.3 N loading rates and characteristics for the DFE and nitrified-DFE effluent.

Component	Annual loading (kg N ha ⁻¹ yr ⁻¹)	Mean concentration (ppm of N)	Range in concentration (ppm of N)
Total organic-N	1119	230	100-430
Ammonium-N	363	53	131-11
Urea-N	72	10.5	0-32
Total for DFE	1554		
Nitrate-N	243	52	33-88
Total for nitrified-DFE	1797		

7.4 Leachate results

The total amounts of ammonium-N, organic-N, and nitrate-N leaching on a kg N ha⁻¹ yr⁻¹ basis for the 12-month period, August 1994 to September 1995, are shown in Table 7.4. As the nitrified-DFE treatments and water controls were not replicated to the same extent as the DFE treatments, statistical analysis is limited to the investigation of treatment effects where drainage had no significant influence.

Table 7.4 Annual ammonium-N, organic-N, and nitrate-N leaching in kg N ha⁻¹yr⁻¹ for various effluent treatments.

Contaminate leaching	Drainage treatment	DFE	Nitrified-DFE	Water
		(kg N ha ⁻¹ yr ⁻¹)	(kg N ha ⁻¹ yr ⁻¹)	(kg N ha ⁻¹ yr ⁻¹)
Ammonium-N	Conventional	23.5	19.7	1.4
	Controlled-low	21.9	18.4	0.9
	Controlled-high	24.2	18.6	1.0
Organic-N	Conventional	161.0	132.1	12.8
	Controlled-low	148.3	141.7	10.2
	Controlled-high	159.2	137.1	13.2
Nitrate-N	Conventional	26.2	59.8	6.3
	Controlled-low	11.0	83.3	2.0
	Controlled-high	3.7	3.7	0.8

7.5 Pasture N uptake

The measured annual pasture N uptake from the lysimeters is shown in Table 7.5.

Table 7.5 Annual pasture N uptake from the lysimeters in kg N ha⁻¹ yr⁻¹

Drainage treatment	DFE (kg N ha ⁻¹ yr ⁻¹)	Nitrified-DFE (kg N ha ⁻¹ yr ⁻¹)	Water (kg N ha ⁻¹ yr ⁻¹)
Conventional	697	836	321
Controlled-low	710	747	444
Controlled-high	705	733	396

7.6 Bromide results

The bromide recovered in the initial leachate event resulting from the irrigations is shown in Table 7.6. The values are presented as a percentage of the bromide applied.

Table 7.6 Bromide recovery in the initial leachate event (approximately 24 hours) after bromide irrigation events, reported as percentage of bromide applied.

Event and irrigation rate (mm h ⁻¹)	Conventional					Controlled-low					Controlled-high				
	Reps			Mean	H ₂ O	Reps			Mean	H ₂ O	Reps			Mean	H ₂ O
	1	2	3			1	2	3			1	2	3		
August 1995 4.9	21.3	15.5	13.3	16.7	20.7	24.8	20.9	15.4	20.4	8.4	19.7	13.6	17.0	16.8	4.1
October 1996 4.9	9.4	3.9	7.2	6.8	5.0	ND	6.1	ND	6.1	7.9	9.4	3.9	4.8	6.0	18.5
October 1996 12.2	23.0	16.4	24.6	21.3	27.5	6.0	17.4	ND	11.7	16.5	12.9	6.9	11.1	10.3	24.2

ND = Not determined

The average mass of bromide recovered with drainage volume in the initial drainage event for the effluent treatments under the 4.9 mm h⁻¹ application rate is shown in Figure 7.2. The October 1996 water-only

conventional and controlled-low data has also been included in the average, as they had similar values of bypass to the DFE treatments.

The final leachate concentrations shown were collected after the lysimeters were allowed to gravity drain overnight. Volume-wise they are consistent with the other sampling points (approximately 500 ml), but there was a 15-hour delay between this sampling point and the previous point, whereas other points were separated by less than 90 minutes.

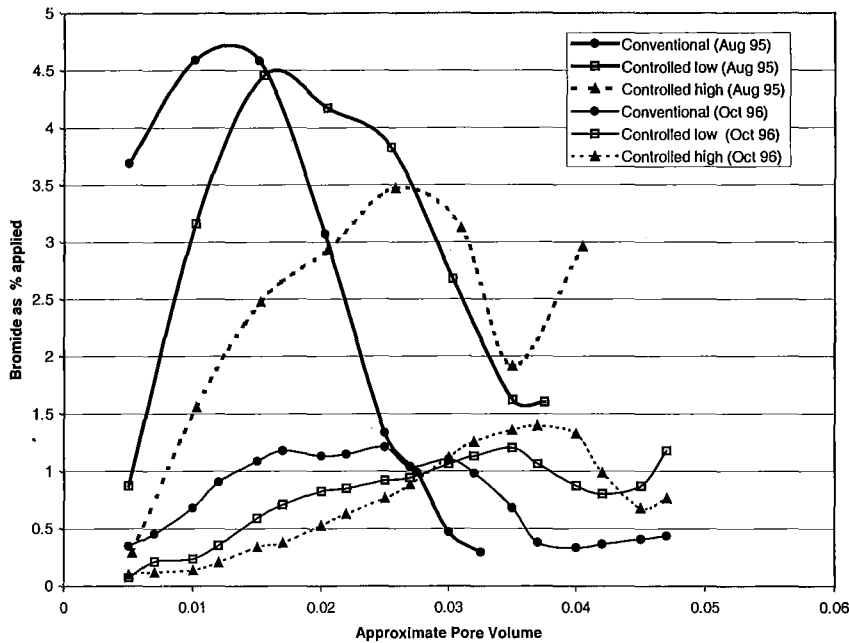


Figure 7.2 Average amount of bromide in drainage water as percentage of the applied bromide in irrigation events in August 1995 and October 1996, at an application rate of 4.9 mm h⁻¹.

Figure 7.3 shows the leachate data for the controlled-low treatment for all four replicates. The water-only treatment had a low bromide breakthrough compared to the three effluent treatments.

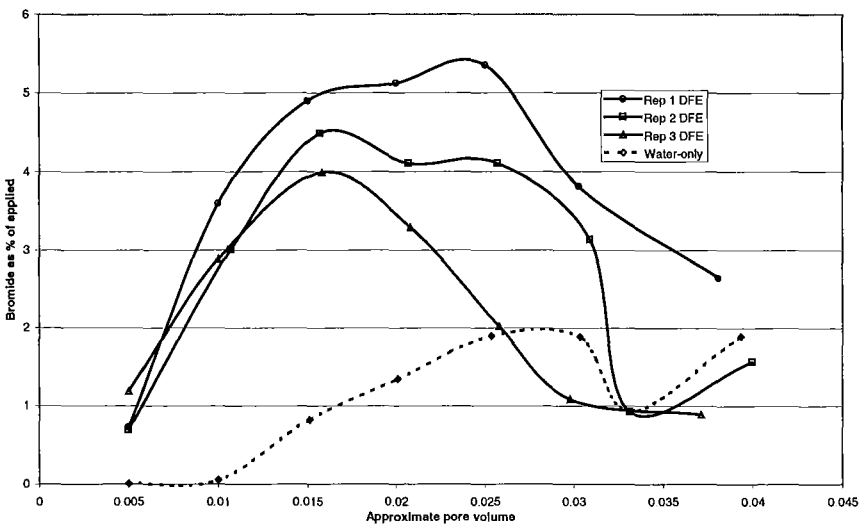


Figure 7.3 Bromide recovery as percentage of applied, for controlled-low drainage treatments.

The average cumulative bromide recovery for the drainage treatments receiving effluent to approximately the two-pore volume depth is shown in Figure 7.4. As the intent was to determine differences in bromide recovery after the initial event, Figure 7.4 does not include the initial breakthrough event.

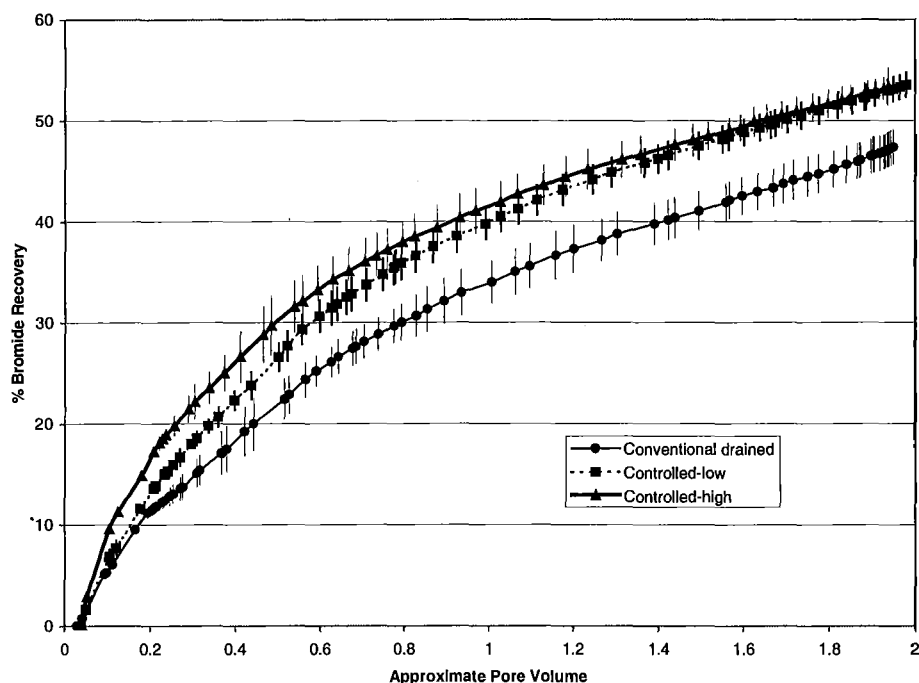


Figure 7.4 Bromide recovery as percentage of applied bromide over two-pore volumes, subsequent to the initial drainage event. Error bars indicate \pm one standard error.

7.7 Discussion

7.7.1 N Leaching

Over all of the effluent drainage treatments the average total N leached in the drainage waters represented approximately 12% of the applied N. This leached N was dominated by organic-N, which ranged between 58% to 87% of the total N leached. Other workers (Cooke *et al.*, 1979; Macgregor *et al.*, 1979) have also found substantial organic-N leaching when DFE was irrigated onto drained soils.

The amounts of ammonium-N and organic-N leached over the year were not affected by drainage treatment (Table 7.4). The nitrified-DFE treatment did have a significantly lower (at 1% level) amount of organic-N and ammonium-N leached compared to the DFE treatment. One possible explanation for this result is that the greater amount of grass growth achieved in the nitrified-DFE treatments decreased the organic-N and ammonium-N lost through bypass flow due to better soil infiltration rates at the soil surface.

The nitrate leaching in the DFE and the water-only control showed the expected trend; the wetter the treatment the lower the amount of nitrate leached (Table 7.4). The nitrate leached in the controlled-high

treatment was only 15% of that leached from the conventionally drained treatment for both the DFE and the water-only treatments.

The nitrified-DFE, however, did not show the same trend in nitrate leaching, the highest amount of nitrate leaching occurred in the controlled-low treatment as opposed to the conventionally drained treatment in the two other cases (DFE and water-only control). The reason for this result can be seen in the nitrate treatment effect on pasture uptake (Table 7.7).

Table 7.7 Treatment effects on leaching and pasture uptake due to additional effluent loading of 243 kg N as NO₃-N.

Effluent treatment	Drainage treatment	Nitrate leaching (kg N ha ⁻¹ yr ⁻¹)	Pasture uptake (kg N ha ⁻¹ yr ⁻¹)
(A) DFE+243 kg NO ₃ -N	Conventional	59.8	836
	Controlled-low	83.8	747
	Controlled-high	3.7	733
(B) DFE	Conventional	26.2	697
	Controlled-low	11.0	710
	Controlled-high	3.7	705
(A-B) Treatment effect	Conventional	33.6	139
	Controlled-low	72.8	37
	Controlled-high	0.0	28

The increase in pasture N uptake (and removal) for the addition of the 243 kg N ha⁻¹ loading of nitrate to the two controlled drainage treatments averaged only 33 kg N ha⁻¹. The conventional drained treatment however had a much greater increase of 139 kg N ha⁻¹. It would seem reasonable that this greater increase in pasture production decreased the amount of nitrate available for leaching from the conventional drainage treatment. If the increased pasture production on the conventionally drained treatment had been of the same order as that on the controlled drainage treatments, then the nitrate leaching would have increased to approximately 140 kg N ha⁻¹. This then would have followed the expected trend for decreased nitrate leaching with increased soil water conditions.

The controlled-high drainage treatment did not show any increase in nitrate leaching with the addition of the 243 kg N ha⁻¹ of nitrate and only a slight increase in pasture production. It could be inferred that the denitrification removal mechanism was very effective in this treatment.

The pasture uptake and removal mechanism accounted for between 40% and 45% of the total applied N in all of the effluent treatments, leaching accounted for another 12% with the remaining 45% either accumulating in the soil profile or lost through gaseous pathways. There was strong evidence from six-monthly soil samplings (data not shown) that total soil N and C values were increasing in the effluent treated lysimeters.

7.7.2 Bromide experiments

The first set of bromide results for August 1995 (Table 7.6) demonstrated the very high amount of bypass flow that was occurring on the effluent treated lysimeters at the time of irrigation. On average 18% of the bromide that was irrigated onto these cores passed through the soil in that one drainage event. The two

controlled drainage water-only lysimeters had a much lower bypass flow component, averaging only 6%. The conventionally drained water-only control however exhibited approximately the same amount of bypass as the effluent treated lysimeters. Particulate matter in the DFE may have reduced soil infiltration rates on the surface, allowing the formation of locally saturated conditions and hence the initiation of macropore or bypass flow. Worm activity could have been increased by a diet of highly organic effluent, potentially increasing bypass flow in the effluent treated lysimeters. Some possible interaction between water table height and worm activity would be needed to account for the larger amount of bypass that occurred on the conventionally drained lysimeter compared to the controlled drainage, on the water-only controls.

The variable results obtained for the bypass flow component of the replicates within a drainage treatment masked any differences that might have been observed between drainage treatments. This result reflects the organic-N and ammonium-N leaching results that were also independent of drainage treatment, as previously discussed.

As most of the N applied was in an organic form (76% and 66% for the DFE and the nitrified-DFE treatments, respectively), and the bypass flow that occurred during an irrigation event was substantial, the predominance of organic-N (81% and 69%) in the leachate was not unexpected.

The bromide data for the drainage within the irrigation event (Figure 7.2) showed that the conventionally drained lysimeters had the highest initial and peak concentrations of bromide. This peak concentration of bromide was also the earliest when compared to the controlled drainage treatments. At the end of the drainage event this conventional drainage treatment also had the lowest concentration of bromide. These effects may be a result of a lack of a water table in the conventionally drained treatments. The water table allows the irrigated bromide to be diluted and hence concentrations (initial and peak) are lower. The passage of the peak bypass was also slowed by the presence of a water table. As wormholes and macropores are already saturated, the advancing bromide must displace this existing water prior to draining. This delays the peak concentration with respect to drainage volume when compared to a profile with no water table. The higher the water table, the greater the volume of water available for dilution and the fuller the macropores, hence the later the peak concentration will occur (Figure 7.2).

The bromide concentrations for the last sample points, which were collected approximately 15 hours after the previous points, were elevated in both controlled drainage treatments but not in the conventional drainage treatment. The explanation for this elevation is that some of the bromide, which had diffused into the immobile region of the soil, had time and opportunity within the saturated region to diffuse out and increase the concentration in the drainage waters. The greater the saturated zone the more the diffusion possible and the more elevated the final sample point. As no water table was present in the conventional drainage treatment no bromide could diffuse out of the immobile region and the last point was not elevated.

Figure 7.3 shows the bromide leaching behaviour with drainage volume for all four replicates of the controlled-low treatment. The water-only control had only 8.4% breakthrough in comparison to the average of 20.3% for the other three effluent replicates. The shape of the curve for the low breakthrough (water-only treatment) was quite different from that of the effluent replicates. The rate of increase in

bromide was much slower and peaked later at a lower value. The final sampling point, which is dominated by diffusion from the immobile region as opposed to bypass flow, was still elevated. The same shape curve is evident in Figure 7.2 for the October 1996 results where the average bypass flow was also comparatively low.

Table 7.8 summarises the impact on bypass flow of the presence (August 1995) and absence (October 1996) of DFE applications and of increasing the application rate from 4.9 to 12.2 mm h⁻¹. With the same application rate, the average bypass flow component on the effluent treated lysimeters had reduced from 17.9% down to 6.4% (significant at the 0.5% level) over the 14-month period when no DFE had been applied. The average breakthrough value for the water-only control stayed approximately the same, but the drainage treatments within the controls change considerably (Table 7.6). The previously high bypass flow component (20.7%) from the conventionally drained treatment reduced down to only 5.0%, while the controlled-high treatment increased from 4.1% to 18.5% and the other treatment remained essentially unchanged.

Table 7.8 **Summary data of mean bromide breakthrough for effluent treatments and water-only controls.**

Event and irrigation rate (mm h ⁻¹)	DFE treatments		Water-only controls	
	Average breakthrough %	Number of reps.	Average breakthrough %	Number of reps.
August 1995 4.9	17.9	9	11.1	3
October 1996 4.9	6.4	7	10.5	3
October 1996 12.2	14.8	8	22.7	3

The decrease in the bypass flow component for the effluent lysimeters at the same application rate can be explained by a decrease in soil infiltration rates, possibly due to effluent clogging the fine pores in the soil, with increased saturation at the soil surface and therefore greater bypass flow. This is the same reasoning for the differences between the water-only and the effluent treatments. Supporting evidence of the changing infiltration rate is that during the August 1995 irrigation there was surface ponding on the lysimeters. However, 14 months later in the October 1996 event there was no ponding present. A possible increase in worm activity through the application of the organic effluent is another contributing factor.

The average of the water-only controls showed very little change in breakthrough value. There were however large changes within the drainage treatments, and this is difficult to explain. One cause may relate to changes in soil properties with time. It does serve to highlight the variable results that can be obtained with saturated water flow.

Increasing the application rate by 2.5 times resulted in approximately doubling of the bypass flow component in both the DFE and water-only control treatments (Table 7.8). This increase in bypass flow was significant (at the 0.5% and 5% levels, respectively) for the DFE and water-only control treatments. During the irrigation at the higher application rate in October 1996 surface ponding existed on the soil surface which obviously increased the bypass flow component. The average bypass flow increased by 17%, 10% and 5% for the conventional drainage, the controlled-low and the controlled-high treatments.

These differences in increased breakthrough between drainage treatments were all significant to at least the 5% level. It is difficult to explain this result, particularly when it applies to the increase in bypass flow associated with a higher application rate and not to the actual amount of bypass occurring.

The cumulative bromide recovery with drainage volume (Figure 7.4) indicates slow diffusion out of the immobile domain of the soil into the drainage water. The recovery of bromide after the first pore volume shows a linear relationship with drainage volume for all drainage treatments. When a water table is present, such as in the controlled drainage treatments, there is a greater recovery of bromide at the same drainage volume compared to the conventionally drained profile. This is due to a larger saturated zone existing and therefore more diffusion occurring from the immobile region into the mobile region which can then be drained from the profile. There is also initial evidence that the greater the saturated zone the greater the bromide recovery, as the controlled-high treatment recovery was initially greater than that from the controlled-low treatment.

7.8 Conclusions

In this study increasing soil water content through the use of controlled drainage reduced nitrate leaching. For effluents where the N composition is dominated by nitrate and sufficient C for denitrification is available, then controlled drainage on these soil types is a feasible treatment option. Increased pasture growth and uptake of N will also reduce nitrate leaching.

The impact on the receiving environment from DFE being applied onto these poorly drained soils is dominated by bypass flow. The amount of bypass flow is not affected by drainage treatment but application rate and history of effluent application will have an influence. Effluents that have substantial particulate matter content may decrease surface infiltration rates, allowing more surface saturation to occur and promoting greater bypass flow. Worm activity (and hence bypass flow) may also increase through the application of organic effluents. DFE treatment systems designed for these soil types need to minimise potential bypass flow by having low application rates, avoiding irrigation when the soil profile is saturated and matching application depths to soil water deficits.

Initial bypass flow and then a slow release from the immobile zone dominate the bromide breakthrough curves which represent the dissolved component of an effluent. The greater the zone of saturation the earlier recovery of the dissolved fractions from the immobile zone, because of the greater opportunity for diffusion. Peak leachate concentration decreased with increasing water table height, but the concentration remained elevated for a longer time period.

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Chapter Eight

Effect of regular irrigation with DFE on soil organic matter and soil microbial biomass

The objectives of this Chapter are to:

Present data on the changes to soil C and N fractions from the repeated irrigation of DFE for testing the CaNS-Eff model

Determine if a single measure of the C_{mic}/C_{org} ratio can be used as an early indicator of long-term change in the total soil C

Provide information on the long-term impact and sustainability of land-applied DFE

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8.1 Introduction

One of the major waste streams of the largest industry in New Zealand, the dairy industry, comes from the cleaning of the milking dairy and associated holding yards on the farm. This very dilute mixture of water, urine and faeces is called dairy farm effluent (DFE). Until recently the main method of disposal of DFE has been two-stage anaerobic-aerobic treatment ponds discharging to surface waterways. Over the last 6 years, however, regulatory authorities have moved to protect surface water quality, and the preferred method of treatment of DFE now is to apply it onto the land (Cameron *et al.*, 1997). Farmers have been relatively quick to adopt this practice. In the Waikato, a major dairying region of New Zealand, the proportion of farmers who land-apply DFE has risen from 35% to nearly 70% between 1993 and 1997 (Selvarajah, 1998).

Typically, 60-85% of the total N (N_t) in DFE is in an organic form (TRC, 1990; Barkle *et al.*, 1994) which is not immediately available for plant uptake. This organic fraction can be conceptually subdivided into an easily mineralisable pool, that becomes available within the year of application, and a more resistant pool, with a mineralisation rate closer to that of native soil organic matter (SOM) (Whitehead, 1995). The rate at which this resistant organic matter from DFE accumulates and the effect of any accumulation on other SOM related pools such as microbial biomass are unknown. This information is necessary to determine the long-term impact and sustainability of applying DFE to land.

Under any given set of environmental and management conditions, soil organic C (C_{org}) and soil organic N (N_{org}) concentrations will equilibrate to a steady-state level reflecting the balance between input and decomposition (e.g. Paul and Clark, 1989). Changes in management result in either an accumulation or a loss of SOM until a new equilibrium is achieved. This may take a considerable time; for example, a new SOM equilibrium was only achieved after 40 years or longer following regular application of farmyard manure (Gutser and Claassen, 1994). Increased SOM concentrations are beneficial with respect to buffering of nutrients, improving soil aggregation and water holding capacity but also result in higher amounts of potentially mineralisable N, which can increase the risk of nitrate leaching (Shepherd *et al.*, 1996). For the Netherlands, it has been estimated that an additional 45-70 kg N ha⁻¹ yr⁻¹ mineralises from SOM accumulated after 20 years of applying slurry manure (Whitmore and Schroeder, 1996).

The high background levels and spatial variation in C_{org} and N_t make changes in these pools difficult to measure in the short term. As an alternative, it has been proposed that a time series of soil microbial biomass determinations (Powlson *et al.*, 1987) or a single measurement of the C_{mic}/C_{org} ratio (Beck, 1984; Sparling, 1992) be used as an early indication of change. While C_{mic} generally only represents 2-5% of C_{org} (Jenkinson and Ladd, 1981), the concept appears sound as the microbial biomass can be regarded as the transformation station through which all organic materials that enter the soil must pass (e.g. Jenkinson, 1988; van Veen *et al.*, 1984). Based on data from long-term field experiments at 26 arable sites in the temperate zone of Central Europe, Anderson and Domsch (1989) report rather constant C_{mic}/C_{org} ratios for a given management regime.

To evaluate the long-term sustainability of the currently recommended DFE irrigation policy the effect of regular irrigation of DFE on SOM must be known. This work reports on changes over four years in C_{org}

and N_t from a soil receiving DFE. Soil microbial biomass measurements were included to test the hypothesis that C_{mic} or the C_{mic}/C_{org} ratio can be used as an early indicator of changes in SOM.

8.2 Materials and methods

8.2.1 Soil lysimeters

This study reports on measurements from the topsoil (0-20 cm) of a lysimeter experiment that investigated the feasibility of using controlled drainage to manipulate soil moisture conditions to enhance denitrification under DFE irrigation. The impact of the DFE irrigation on N leaching and pasture production has been reported previously (Barkle *et al.*, 1998a, 1998b; Singleton *et al.*, 2000). As details of the experimental set-up have been reported there, only a brief description is presented here.

Twelve undisturbed soil lysimeters (0.6 m dia. by 1.2 m deep) were collected, based on the method of Cameron *et al.* (1992). They were replaced in the ground around a buried access chamber where the leachate was collected. Three drainage treatments were investigated. In the conventional drainage treatment the maximum depth to the water table was 75 cm from the surface. The two other treatments had drainage control, which only allowed drainage to occur when a water table depth of 50 or 25 cm from the soil surface was reached. Three replications of each drainage level were irrigated weekly with fresh DFE over the milking season. One lysimeter of each drainage treatment was irrigated with water only ($< 0.01 \text{ mg N l}^{-1}$) and acted as a water-irrigated control treatment. The Te Kowhai silt loam used is widespread in the Waikato. It is classified as a Typic Orthic Gley soil in the New Zealand Soil Classification (Hewitt, 1992) and as a Typic Ochraqualf in Soil Taxonomy (Soil Survey Staff 1990). The particle size distribution in the topsoil (0-22 cm) is 36% clay, 55% silt, and 9% sand. Average total soil C prior to treatment was 3.54% and total N 0.34%.

8.2.2 Effluent irrigation

Effluent was collected on the day of irrigation from the dairy washings at Number 1 Dairy, Ruakura Research Centre, Hamilton. Effluent was irrigated weekly over the milking season for 8 months in the first year (September 1992 to April 1993), for 9 months in the second (August 1993 to April 1994) and for 10 months in the third year (August 1994 to May 1995). An irrigation depth of 17 mm, equivalent to about half the available water storage of the topsoil (0-20 cm), was used as the weekly irrigation volume. In the second and third year, the effluent N concentration was increased by adding fresh faeces and urine in amounts that maintained similar N proportions to that of the effluent applied in the first season (Table 8.1).

Table 8.1 Annual C and N loadings (kg ha⁻¹) during the three years of effluent irrigation.

Period	DFE				Clippings in DFE treatment		Clippings in control	
	C _{org}	NH ₄ -N	N _{org}	N _t	C _{org}	N _{org}	C _{org}	N _{org}
Year 1	5768	133	377	510	4830	341	4100	418
Year 2	21661	285	1234	1519	-	-	1780	152
Year 3	9697	435	1119	1554	-	-	3543	233
Total	37126	853	2730	3583	4830	341	9423	803

8.2.3 Pasture management

The ryegrass-clover pasture on the lysimeters was cut approximately every 28 days to represent a “typical” dairy grazing rotation in the Waikato. Approximately half the pasture samples were returned to the respective lysimeters in the first year (Table 8.1). This is a technique often used in field mowing trials to simulate grazing (Roberts, A.H.C., 1992, pers. comm.). In the second year, clippings were not returned to lysimeters irrigated with DFE. This was to simulate a “cut and carry” system of N removal in pasture, as may be recommended to prevent nitrate leaching under high effluent N loading rates (O’Conner *et al.*, 1998).

8.2.4 Soil moisture data

Soil moisture data in 10 cm increments beginning at 5 cm from the soil surface were measured using a Troxler Model 3221 Neutron Probe on a weekly basis from September 1992 to February 1995. The conversion equations were based on measured soil properties (bulk densities and loss-on-ignition data) and calibration measurements which included this soil type.

8.2.5 Sampling and analysis

At each sampling date, three small soil cores 2.5 cm diameter (0.5% of lysimeter area) to 20 cm depth were collected from each lysimeter. These cores were subdivided into three layers, 0-5 cm, 5-10 cm, and 10-20 cm. The holes in the lysimeters were repacked with soil from the same depth collected in the field. Samples were taken before the start of effluent irrigation (July 1992) and about 6-monthly from January 1993 to January 1995 and after the last irrigation period (July 1995 to August 1996). The sampling in the latter period was undertaken to see if parameters changed by the effluent irrigation would move back to original levels after the end of effluent irrigation, and thus indicate the resilience of the system. In the effluent treatment (DFE), the 3 replications of each drainage level were bulked prior to analysis until January 1995. Thereafter, the samples from each lysimeter were analysed separately. In the water-irrigated control treatment (W), the samples from the three water table levels had also been bulked until January 1995. Samples of each lysimeter were analysed separately thereafter to check for possible differences between the water table levels. As no significant differences were found between the three water table levels of the water- or effluent-irrigated lysimeters, only the means of the DFE or W treatments are

presented. For the samplings beginning with January 1995, differences between the effluent and the control treatment were tested using the least significant difference approach at $P = 0.05$.

Total C concentrations of finely ground samples were measured according to standard procedures (Blakemore *et al.*, 1987), using a Leco induction furnace. As there is no free carbonate in the soil used, the value obtained was taken as the total organic C (C_{org}) concentration of the soil. Total N was determined by a modified semi-micro Kjeldahl digestion method (using salicylic acid to include nitrate) and auto-analyser as described by Blakemore *et al.* (1987). Soil microbial biomass-C was measured using the substrate-induced respiration (SIR) method (Anderson and Domsch, 1978), in the modified version of Sparling and West (1988). The revised calibration of Sparling *et al.* (1990) was used to calculate microbial C (C_{mic}). Basal respiration measurements followed the method of Sparling *et al.* (1986), leaving the soil samples at their original moisture concentrations. The pH of the soil samples (soil:water ratio of 1:2.5) was measured with a Triac pH meter.

8.3 Results

8.3.1 Total organic C and total N

After 2 years of effluent irrigation, the mean total organic C (C_{org}) concentrations in all 3 layers were consistently higher than those of the water treatment (Figure 8.1a). However, due to the high variability, these apparent differences were only statistically significant in January and August 1996 in 0-5 and 5-10 cm depth of soil, and in July 1995 and August 1996 in 10-20 cm depth of soil. C_{org} concentrations at the end of the effluent irrigations (July 1995) were significantly higher than initial concentrations (July 1992) in the 5-10 and 10-20 cm depths and remained so until the end of the study (August 1996).

The dynamics of total N concentrations (N_t) were similar to those of C_{org} (Figure 8.1b), with statistical differences between effluent and water treatments only significant in July 1995 (10-20 cm), January 1996 (0-5, 5-10 cm) and in August 1996 (5-10 cm). By July 1995, the end of the effluent irrigation, the N_t concentrations were significantly higher than those of July 1992 in 0-5 and 5-10 cm depths of soil, but, unlike C_{org} , dropped to initial levels after the end of the effluent irrigation.

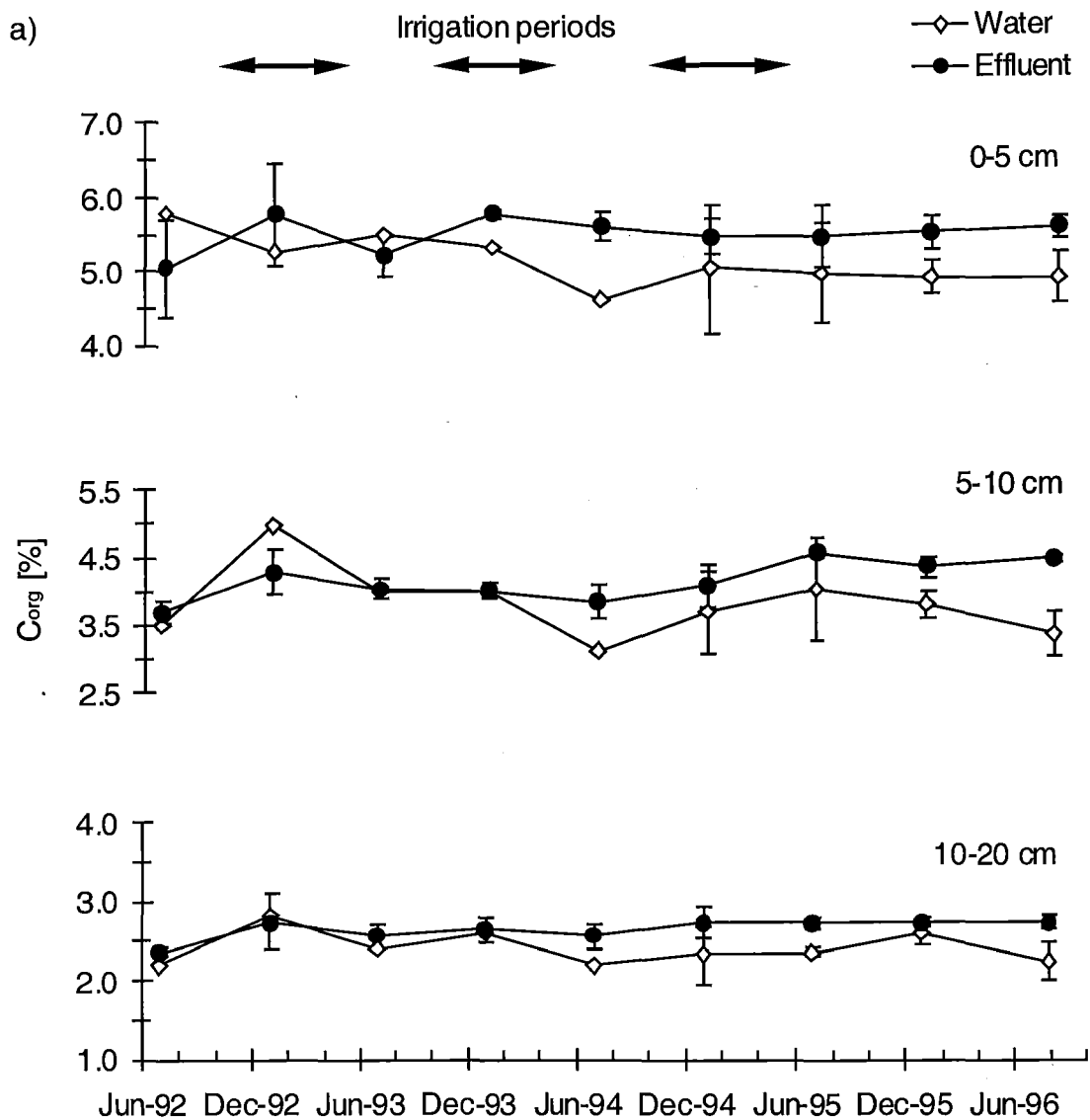


Figure 8.1 (a) Dynamics of organic C (C_{org}) in 0-5, 5-10, and 10-20 cm depths of soil.

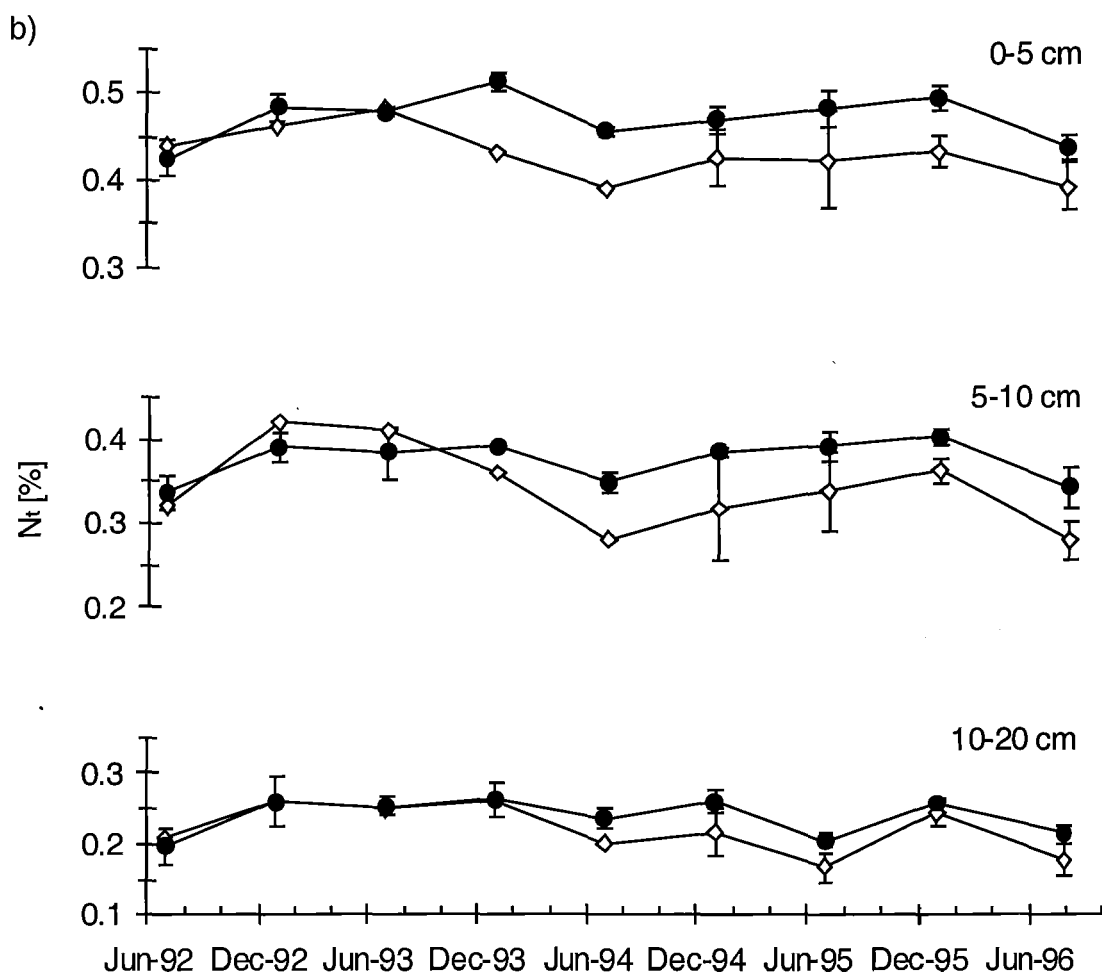


Figure 8.1 (b) Dynamics of total N (N_t) in 0-5, 5-10 and 10-20 cm depths of soil.

8.3.2 Soil microbial biomass (C_{mic})

Beginning in July 1993, C_{mic} concentrations in the effluent treatment were consistently higher than in the water treatment (Figure 8.2a). Only one difference was found to be not statistically significant (January 1996, 10-20 cm) during the period when the l.s.d. test could be applied (beginning in July 1995). C_{mic} concentrations at the end of the effluent irrigations were significantly enhanced in all 3 soil layers compared to initial concentrations. In the uppermost 2 layers, C_{mic} concentrations declined significantly thereafter and were similar to initial values in January and August 1996, whereas the C_{mic} concentration of the lower layer remained enhanced.

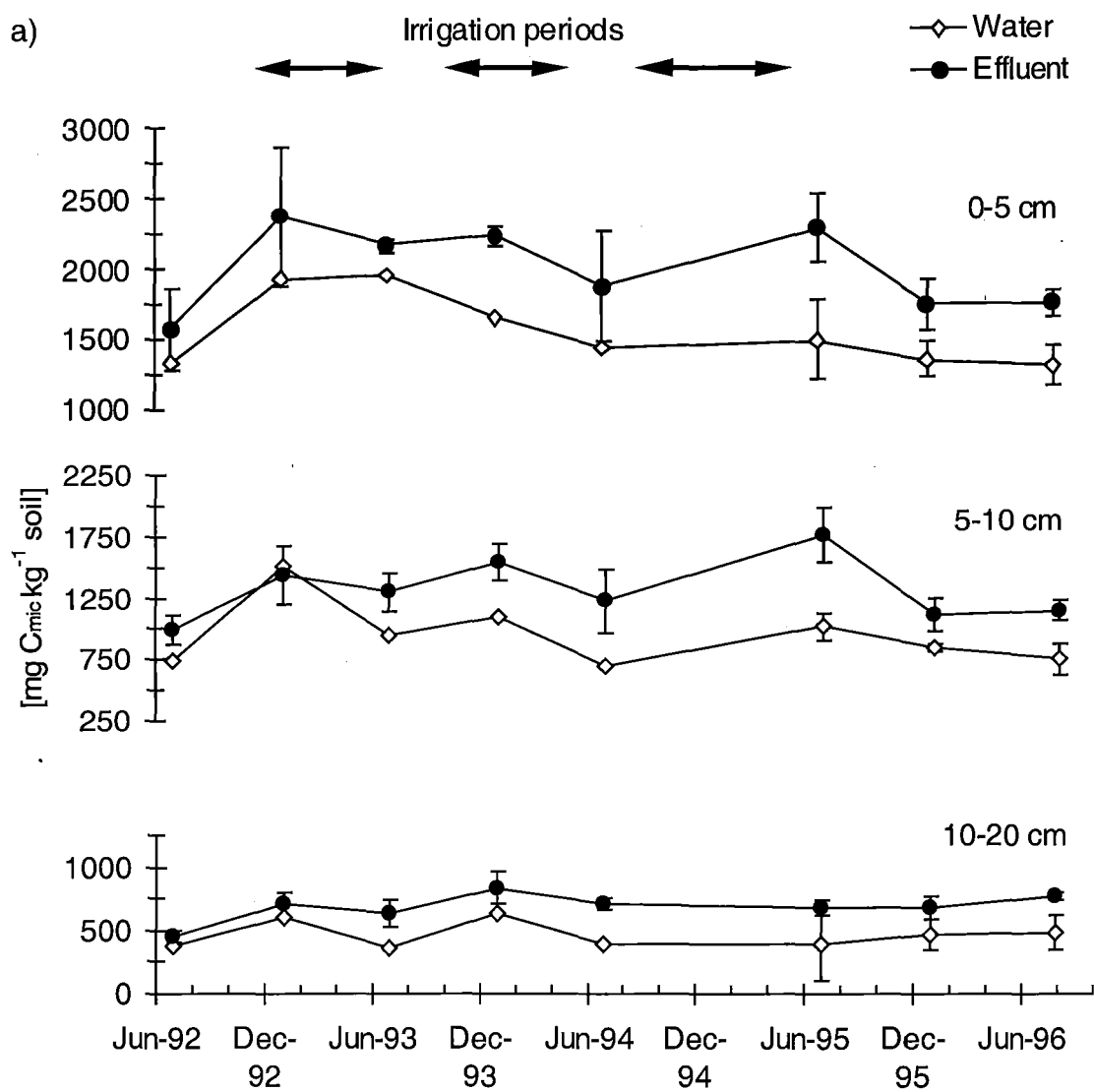


Figure 8.2 (a) Dynamics of microbial C (C_{mic}) in 0-5, 5-10 and 10-20 cm depths of soil.

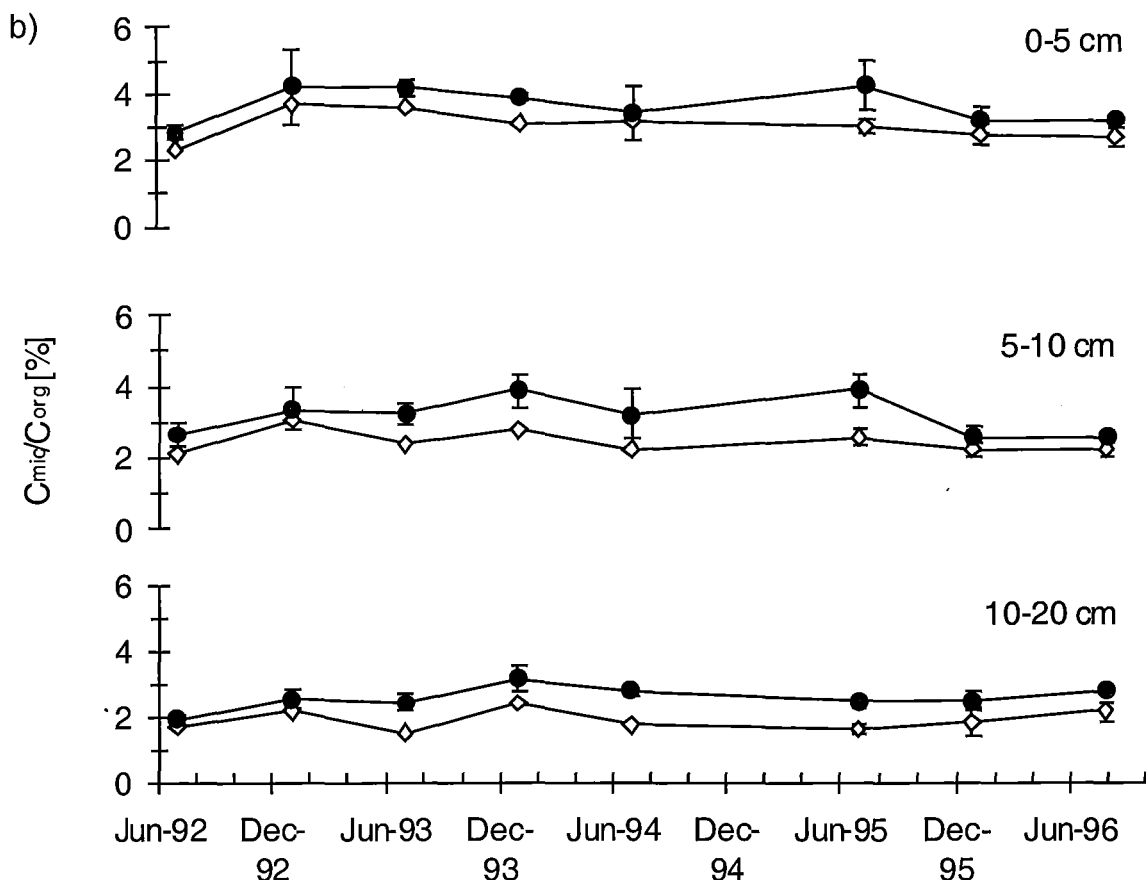


Figure 8.2 (b) Dynamics of the C_{mic}/C_{org} ratio in 0-5, 5-10, and 10-20 cm depths of soil.

8.3.3 C_{mic}/C_{org} ratio

Between July 1995 and August 1996 the C_{mic}/C_{org} ratio was significantly higher in the effluent-irrigated treatment than in the water treatment, with the exception of the 0-5 and 5-10 cm layers in January 1996 (Figure 8.2 b). In July 1995, shortly after the end of the effluent irrigation, the ratio was 4.2% in 0-5, 3.9% in 5-10 and 2.5% in 10-20 cm depth of soil. These ratios were significantly higher than the initial values which were 2.9% at 0-5, 2.7% at 5-10 and 1.9% at 10-20 cm depth. After the end of the effluent irrigation, the ratio dropped back to initial levels in 0-5 and 5-10 cm depths of soil, but remained enhanced in 10-20 cm depth.

8.3.4 Basal respiration

Basal respiration (data not shown) strongly followed the same dynamics as the water content of the soil sample. Correlation analysis showed that soil moisture could explain 63% of the variation in the basal respiration data at the 0-5 cm depth, 56% at 5-10 cm and 37% at 10-20 cm. Differences between the treatments were significant in July 1995 and August 1996 in the 5-10 and 10-20 cm layers.

8.3.5 Soil moisture

The soil moisture data, as percentages of saturation, show that differences between the effluent and the water treatments occurred only during the relatively dry periods (Figure 8.3). During these periods, the effluent treatment, which had more pasture production, was the drier treatment. The difference in soil moisture was greater near the soil surface and depended on the seasonal rainfall and evapotranspiration.

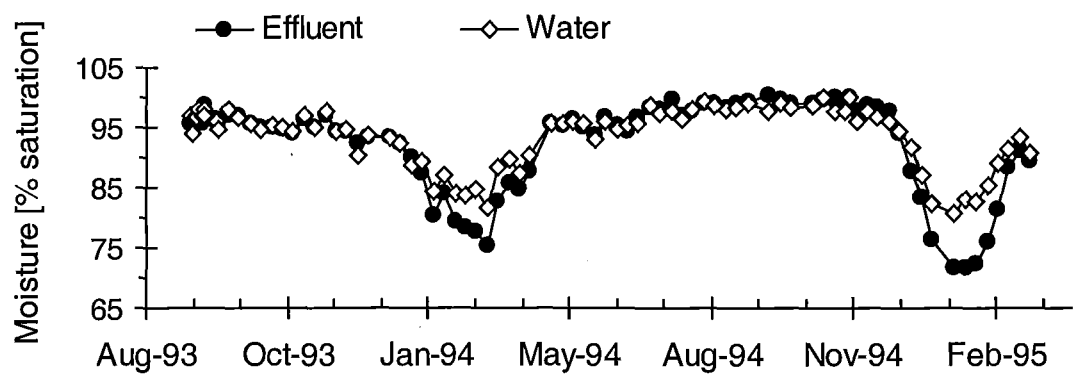


Figure 8.3 Dynamics of soil moisture at 5 cm depth of soil.

8.3.6 pH value

Higher pH values in the effluent-irrigated soils become apparent in January 1994, during the second year of irrigation (Figure 8.4). The differences from the water-treatment values were statistically significant in all 3 layers in July 1995 and August 1996. The pH values in the effluent treatment in July 1995 were higher than before effluent irrigation, but had dropped back to initial values by the end of the measurements. In August 1996, pH values in the water-irrigated treatment were slightly below initial values.

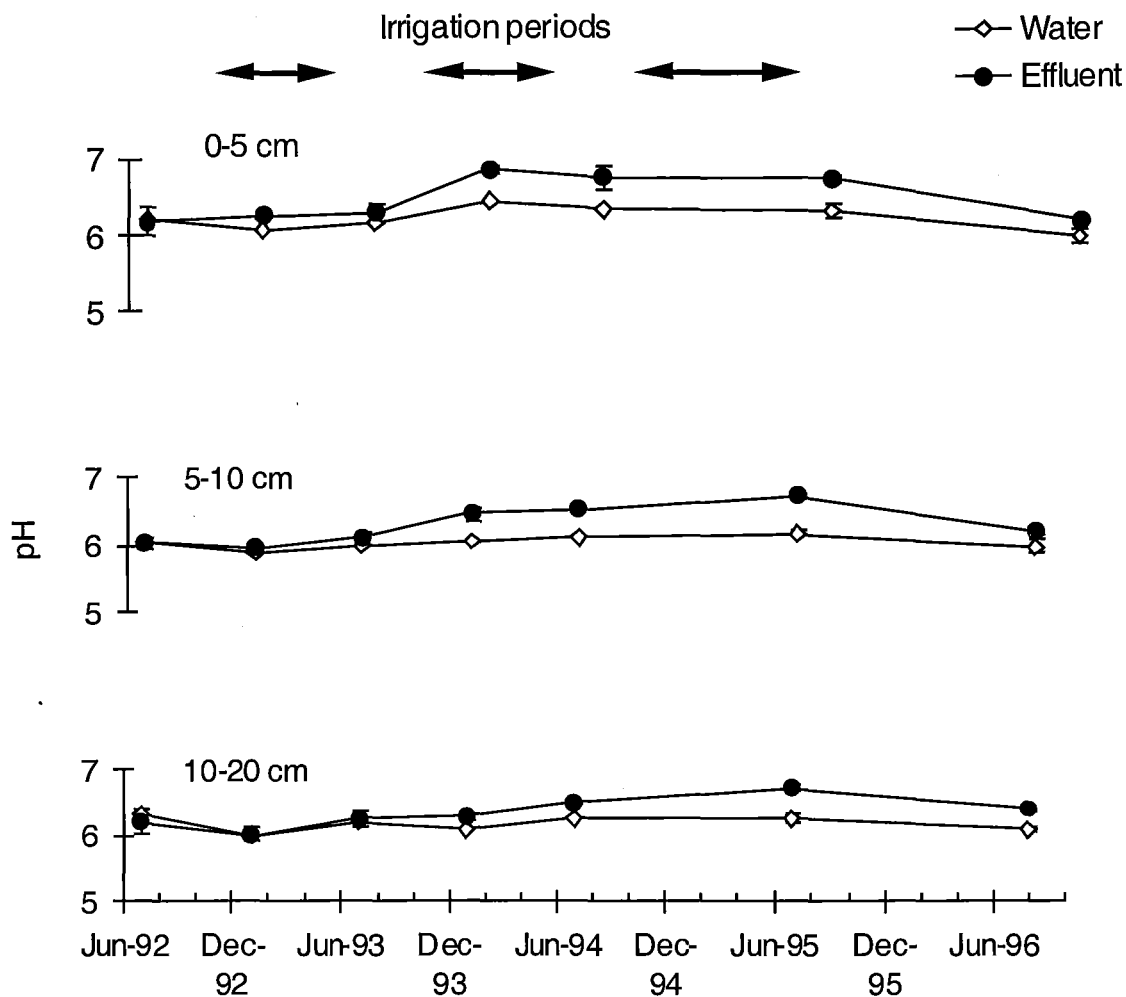


Figure 8.4 Dynamics of the pH value in 0-5, 5-10, and 10-20 cm depths of soil.

8.4 Discussion

8.4.1 Soil C and N

Cameron *et al.* (1997) stated that the annual rates of organic matter input in effluent treatment systems are generally regarded as too low to cause a significant increase in SOM. In this study however, with the high loading rates of about 42000 kg C ha⁻¹ and 3900 kg N ha⁻¹ applied over 3 years as DFE and, to a minor extent, in the returned pasture clippings, there was a significant increase in C_{org} and N_t. As land application of DFE was not a widespread treatment practice until recently, there is a lack of long-term data on the effect of the lower recommended application rates on SOM. However, more than 20 years of irrigation with untreated meatworks effluent increased C_{org} from 5.6% to 6.8% (Ross *et al.*, 1982).

While the applied amounts were almost 9 times as high as the recommended maximum for grazed pasture of 150 kg N ha⁻¹ yr⁻¹ in the Waikato, the increases in C_{org} and N_t between the water- and effluent-irrigated treatments were only statistically significant in some instances. This reflects in part the small-scale spatial variation that cannot be overcome when only small samples can be taken from the lysimeters in order to keep them as undisturbed as possible over the whole experimental period. Moreover, possible seasonal

variations of soil organic matter (e.g. Leinweber *et al.*, 1994) may cause some scattering of the time series rather than the expected steady increase with increasing amounts of effluent applied. It is noteworthy that C_{org} and N_t concentrations developed differently after the end of the effluent irrigations. Whereas C_{org} concentrations remained at the level of July 1995, N_t concentrations in 0-10 cm depth of soil dropped significantly until August 1996, indicating higher mineralisation of the accumulated N_t compared to the accumulated C_{org} .

8.4.2 Soil microbial biomass (C_{mic})

The water-irrigated treatment showed an initial increase in C_{mic} when irrigation was started, which was supposedly due to more favourable moisture conditions for soil microorganisms. Whereas C_{org} and N_t concentrations consistently differed between the water- and effluent-irrigated treatments beginning in July 1994, two years after the start of effluent irrigation, the C_{mic} data indicated consistent differences one year earlier. This quicker response to changed management is also obvious after the end of the irrigations in July 1995. Whereas the drop in N_t concentrations became significant after 12 months, the decline in C_{mic} was significant in the first 6-monthly sampling after the end of the irrigations. It could be suggested that the drop in C_{mic} concentrations from July 1995 to January 1996 was induced by the strong decrease in soil moisture during the summer period (data not shown). However, the moisture concentrations in January 1996 were similar to those in January 1993 and January 1994 when increases in C_{mic} concentrations were measured.

8.4.3 C_{mic}/C_{org} ratio

The C_{mic}/C_{org} ratios in both treatments showed a gradual decrease from the 0-5 cm surface layer to 10-20 cm depth. The mean C_{mic}/C_{org} ratios of the water-irrigated treatment (July 1992 excluded) were 3.1% for 0-5, 2.5% for 5-10, and 1.9% for 10-20 cm soil depth. This gradient is thought to be mainly the result of a decreasing proportion of readily decomposable organic matter, suitable to sustain soil microbes, in the total SOM pool as well as less favourable environmental conditions for microorganisms in the lower layers. As outlined earlier, the determination of a single C_{mic}/C_{org} ratio was proposed to ascertain whether a soil had achieved equilibrium in soil organic matter status under a given climatic and land-use regime. However in contrast to the rather constant C_{mic}/C_{org} ratios reported by Anderson and Domsch (1989), Sparling (1992) reported a wide range of 0.99% to 4.30% in the C_{mic}/C_{org} ratio of 22 samples taken from 0-7.5 cm depth from long-term New Zealand pasture soils. To allow a comparison with these data, the weighted average for a 0-7.5 cm sampling increment was calculated. This C_{mic}/C_{org} ratio of 2.9% for the water-irrigated treatment was somewhat higher than the median of the ratios reported by Sparling (1992).

Anderson and Domsch (1989) reported enhanced C_{mic}/C_{org} ratios for arable plots that had received organic fertiliser the year prior to sampling. However, even our highest ratio of 4.2%, measured in the uppermost 5 cm of the DFE-irrigated treatment after three years of irrigation with high loading rates, was within the wide range reported by Sparling (1992). Due to this high variation among soils and management treatments, a single determination of the C_{mic}/C_{org} ratio cannot be used as an indicator of change, unless the baseline C_{mic}/C_{org} ratio prior to the change in management is known. As Sparling (1992) summarised, it has been found that clay content, mineralogy, organic matter, vegetation, time of sampling and

management history affect the C_{mic}/C_{org} ratio. As the gradient with soil depth found in this study emphasises, sampling depth also would have to be standardised. Consequently, a single determination of C_{mic}/C_{org} is of little value unless a comprehensive database of reference values has been established. The repeated determinations of the C_{mic}/C_{org} ratios with time did not yield any further information than the C_{mic} data alone, indicating that additional measurement of C_{org} is not necessary.

8.4.4 Soil pH

The soil pH was increased by approximately 0.5 in all three sampling depths due to DFE irrigation. This result is consistent with other studies. For example, soil pH increased by 0.5 on irrigation with secondary-treated sewage effluent (Kim and Burger, 1997; Falkiner and Smith, 1997) and by 0.6-1.0 with tertiary-treated effluent (Schipper *et al.*, 1996; Magesan *et al.*, 1999). This effect on soil pH is favourable for soil microbial activity and reduces the need for regular liming.

8.5 Conclusions

This work has shown that regular irrigation with DFE at the high loading used in this study will at different rates increase the C_{mic} , pH, C_{org} , and N_t of the soil receiving the effluent.

After sustained changes in land use or management practices, where a change in soil organic matter can be expected in the long-term, a single determination of the C_{mic}/C_{org} ratio can not be used as an early indicator of changes in C_{org} and N_t . This ratio becomes suitable however, if it is compared to an initial value. The same information can be deduced from the change in C_{mic} concentration alone, meaning the additional determination of C_{org} is not necessary.

The long-term sustainability of DFE application onto land can be maintained only when the supply of inorganic N is continually matched by the demand of the pasture. This means that inorganic fertilisation has to be reduced concurrently with the gradually increasing N mineralisation from the accumulating organic matter. In ryegrass-clover pastures however, the increased mineralisation may be offset by reduced N-fixation (Di *et al.*, 1998).

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Chapter Nine

Hydrology models DRAINMOD and SWIM applied to large soil lysimeters with artificial drainage

The objectives of this Chapter are to:

Modify the SWIM model so it can simulate controlled drainage

Compare the predicted with measured drainage fluxes of the two hydrological models to select a preferred model to use with CaNS-Eff

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9.1 Introduction

The ability to predict soil water distribution and movement accurately is critical for the realistic estimation of most biological and plant processes within the soil system. The prediction of leachate movement is also fundamental for describing the transport and fate of applied nutrients and chemicals in the soil.

The most exact approach for the prediction of both vertical and lateral water fluxes in the soil profile is to solve the 2-dimensional form of Richards' equation for saturated and unsaturated flow. However this approach is difficult to use and computational requirements generally limit its application to short-term events or testing of approximate methods (Karvonen and Skaggs, 1993).

Richards' equation is the combination of the water conservation equation which relates water fluxes, storage changes, and inputs and/or losses with the Buckingham-Darcy flux equation. The resulting equation has two unknowns, the matric potential (ψ) and water content (θ). One of these two unknowns can then be eliminated by using a measured soil relationship between matric potential and water content. By eliminating matric potential a water content form of the Richards' equation results which is a second-order, nonlinear partial differential equation generally solved by numerical methods.

Simulation models such as SWIM (Ross, 1990a), PREFLO (Workman and Skaggs, 1990) and SWATREN (Vanclooster *et al.*, 1994) have been developed as 1-dimensional implementations of Richards' equation with a fixed finite difference grid. If required, drainage theory is then used to determine fluxes within the saturated zone. Some numerical solutions to Richards' equation use adaptive spatial resolution, e.g. WAFLOWM (Dane and Mathis, 1981), or adaptive spatial and temporal resolution, e.g. RZWFL0 (Johnsen *et al.*, 1995).

Alternatives to the Richards' equation to predict soil water distribution have also been developed. For example, DRAINMOD (Skaggs, 1980b) and ADAPT (Desmond *et al.*, 1996) both use a lookup table relating the volume of soil water or air in the profile to the depth of the saturated zone. The soil water in the unsaturated zone is assumed to be at "equilibrium", that is, there is a 1:1 increase in matric potential with distance from the saturated zone to the soil surface. This equilibrium condition is assumed to exist up to the soil surface provided that the soil evaporative and plant water demands can be met by upward flux from the water table. If the upward flux cannot satisfy these demands, then a "dry zone" is simulated. In this zone, soil layers from the surface down to the bottom of the rooting zone are sequentially dried to the soil's wilting point content. When subsequent rainfall occurs, the infiltrating water is considered to increase the soil water in the dry zone. The inputs (irrigation and rainfall) and losses (ET, drainage, and seepage losses) from the soil profile are tracked in a water balance equation. The output variable in the balance equation, which is the change in the soil air volume, is used as the key to determine the location of the saturated zone using the lookup table. The use of the water balance equation in the process leads to these models being referred to as "water balance models".

Other models such as EPIC-WT (Sabbagh *et al.*, 1993) and GLEAMS-WT (Reyes *et al.*, 1994) fill the soil profile layer by layer, up to the field capacity, from the soil surface downwards with the infiltrating water. This approach is often referred to as a "tipping bucket" model. If the water reaches the saturated zone, then the water table rises by the appropriate infiltrating amount. Drainage fluxes, deep seepage and

upward flux all cause the water table to be drawn down. Plant water uptake and surface evaporation demands are determined on a layer by layer basis within the rooting zone.

Both “water balance” and “tipping bucket” as described above are simpler and are much less computationally intensive than solving the Richards’ equation. However, minimising the cost in loss of accuracy depends on the validity of the simplifying assumptions. When soil conditions match the simplifying assumptions then agreement with predictions from Richards’ equation is generally good. However, when the assumptions are violated for significant periods, larger differences between the two approaches are apparent. In a comparison between DRAINMOD and a model using a solution to Richards’ equation, Karvonen and Skaggs (1993) found that for soils with a large hydraulic conductivity the water table results predicted by the two methods were generally in good agreement. The greatest deviation occurred when the soil had small hydraulic conductivity and climatic conditions were dry. These conditions violated DRAINMOD’s inherent assumptions.

When two or more models are considered as suitable for a given simulation task, a common approach to selecting the most appropriate model is to evaluate the predictions of both models against measured data. It is desirable that the measured data are similar to the conditions which are expected in the actual simulation task. Any differences between the predicted and measured values can originate from three sources: uncertainty in the model parameters, errors in the input data or measurements themselves, and differences due to the equations within the models not adequately representing the physical processes.

Although input parameters may vary between the models, due to the different process equations being used, the data set used to derive the parameters for both models should be the same. Different models may subsequently put more weight on different processes, depending on the model structure. Provided that the data set from which the parameters are estimated is similar to that which will be used in the actual simulation task, any differences between simulation results are a valid outcome of the selection process and reflect the likely adequacy and suitability of each model for the required task, given the nature of input data set available.

The third source of differences occurs when an algorithm or method within a model may be inappropriate or less accurate than another model’s implementation. The comparison process as described, where predicted values from the two models are compared against a measured data set, is a valid test of the overall suitability of each model. This Chapter describes the application of such a selection process to 2 hydrological soil water models to determine the most appropriate model for the prediction of soil water movement.

In other published comparison studies of hydrological models for similar data sets (Table 9.1), the typical standard error in the prediction of water tables is similar for both Richards’ and alternative type models, approximately 0.18 m. Standard errors (SE) are calculated as:

$$SE = \sqrt{\frac{\sum (Mea. - Pred.)^2}{n}} \tag{9.1}$$

Table 9.1 **Comparison of model studies from various sites, intervals generally daily.**

Reference	Years of site data	Model		Water table standard error (m)	Total drainage measured/predicted	
					Surface	Subsurface
<i>Aurora; North Carolina, USA</i>						
Desmond <i>et al.</i> (1996)	5	ADAPT	(B)	0.18		
Johnsen <i>et al.</i> (1995)	3	RZWFLO	(RA)	0.17		
	3	WAFLOWM	(RA)	0.17		
Skaggs (1982)	5	DRAINMOD	(B)	0.15		
Workman and Skaggs (1989)	5	SWATREN	(R)	0.18		
Workman and Skaggs (1991)	5	PREFLO	(R)	0.17		
<i>Ben Hur; Louisiana, USA</i>						
Sabbagh <i>et al.</i> (1993)	7	EPIC-WT	(B)	0.25 ^A	1.31	1.20
		DRAINMOD	(B)	0.20 ^A	1.07	1.33
Reyes <i>et al.</i> (1994)	7	GLEAMS-SWAT	(B)	0.19 ^B	0.94	0.99
Fouss <i>et al.</i> (1987)	3	DRAINMOD	(B)	0.17	1.08	1.28
<i>Waikato, New Zealand</i>						
This study	4	DRAINMOD	(B)	0.12		0.95
		SWIM	(R)	0.09		1.10

^A Standard deviation

^B Average deviation

Values are averages or typical values for each study. Model types: B, Balance; R, Richards’ equation; RA, Richards’ equation adaptive grid

The predicted total surface drainage from the “water balance” and “tipping bucket” models is typically over-estimated by 10% (Table 9.1). Surface drainage occurs when water is lost from a site in overland flow, as opposed to subsurface drainage where water moves through the soil profile into an artificial drainage pipe. Subsurface drainage is generally over-predicted by approximately 20%.

9.2 Lysimeter information

Nine undisturbed soil cores (0.6 m dia. by 1.2 m deep) of Te Kowhai soil were collected using the method of Cameron *et al.* (1992). This method employs a sealant of molten petroleum jelly between the lysimeter casing and the soil core itself. This seal is intended to prevent any undesirable preferential flow of water between the lysimeter casing and the soil core.

Outlets (drainage tubes) were installed at 0.75 m from the soil surface, just above or on the slowly permeable layer (Figure 9.1). Control of the water table within the lysimeters was achieved by installing a weir in the outlet tube. The weir prevents discharge from the lysimeter until the water table inside the lysimeter had risen to the height of the weir. The maximum height that the saturated zone within the lysimeters could achieve was to the height of the weir. The different soil drainage treatments within the lysimeters were imposed by having two weir heights. The three drainage treatments investigated on these lysimeters are shown in Table 9.2. Each drainage treatment was replicated 3 times. Pressure sensors were installed in the drainage tubes of the controlled drainage treatments to record on a 3-hourly basis the height of any water table.

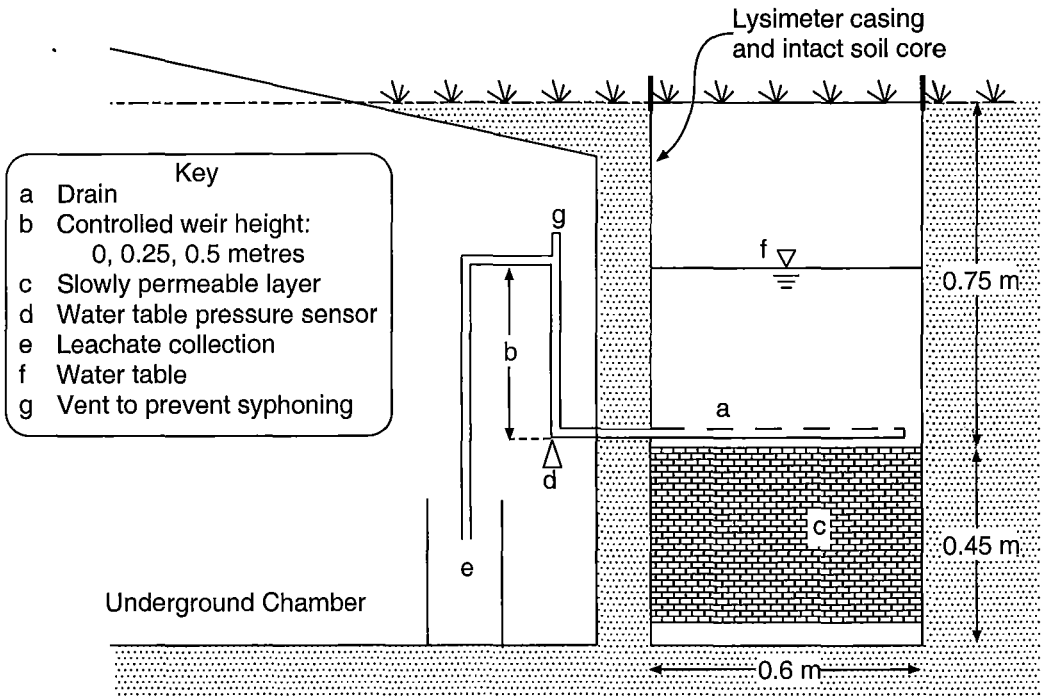


Figure 9.1 Lysimeter configuration.

Table 9.2 Drainage treatments imposed on lysimeters.

Drainage treatment	Height of weir (m) in outlet tube above the impermeable layer	Max. depth (m) to water table from the soil surface
Conventional drainage	0	0.75
Controlled-low	0.25	0.50
Controlled-high	0.50	0.25

The lysimeters were irrigated with a very dilute organic slurry once a week from September through to May, from 1992 to 1996. This application regime was varied in October and November 1995, when additional clean water irrigations were used to investigate solute movement in the lysimeters. All effluent or water applications were to a 17 mm depth over a 3 ½ h period. The application method, which used a rose-head sprinkler coupled to a solenoid valve mounted beneath individual buckets, simulated a sprinkler irrigation system. The irrigation rate, derived from the unsaturated hydraulic conductivity ($\psi = -40$ mm) of the topsoil, was chosen to avoid surface ponding and minimise preferential flow. The leachate from the lysimeters was generally collected on a daily basis. A ryegrass-clover (*Lolium perenne* L. / *Trifolium repens* L.) pasture mix was grown on all lysimeters under a harvesting regime where pasture was cut and removed every 28 days.

Hourly rainfall data were obtained from the Ruakura meteorological station (C75731) some 300 m from the experimental site. The potential evapotranspiration (PET) was estimated using the Priestley Taylor method (Priestley and Taylor, 1972), using temperature and solar radiation data from the same meteorological station. The annual quantities of rainfall, irrigation, and potential evapotranspiration are given in Table 9.3.

Table 9.3 Annual rainfall (R), irrigation (I), and potential evapotranspiration (PET) at the lysimeter site, all measurements are in mm

Year	Rain (R)	Irrigation (I)	PET (P)	Inputs (R+I)	Drainage (R+I-P)
1992 ^A	770	301	488	1071	583
1993	872	691	1030	1563	533
1994	1047	705	1065	1752	687
1995	1341	894	1016	2235	1219
1996 ^B	737	69	524	806	282

^A Last six months

^B First six months

9.3 Soil properties

The soil used in the lysimeters was Te Kowhai silt loam, which is classified as a Typic Orthic Gley (Hewitt, 1992), (New Zealand Classification) or a Typic Ochraqualf (Soil Survey Staff, 1990), (USA Classification). The texture is silt loam to about 0.7 m and then silty clay to the base of the slowly permeable layer at about 1.1 m, with sands beneath. Wormholes and partings between aggregates extend to depths greater than 0.6 m (P.L. Singleton and G.F. Barkle, unpublished data). In the field, water perches on the slowly permeable layer for several months of the year (Singleton, 1991a, 1991b). Soil physical properties obtained at the time of collection of the lysimeters are summarised in Table 9.4.

Table 9.4 Properties of Te Kowhai soil used in the irrigated lysimeter study.

Horizon ^A	Depth (m)	Clay (%)	Total porosity (%)	Macro porosity (% v/v)	Field capacity (% v/v)	Hydraulic cond. (mm h ⁻¹)			Sat. perm class
						K _{sat}	K _{20 mm}	K _{40 mm}	
Apg	0.0-0.05	38	56.7	6.7	48.6	11.3	6.8	3.1	Mod. rapid
Ap	0.05-0.2	40	53.2	10.4	40.9	119.3	16.8	8.1	Very rapid
BgC	0.2-0.3	39	54.5	15.4	37.6	510.5	23.1	20.0	Very rapid
Br1 upper	0.3-0.4	30	56.7	11.0	43.5	3.4	1.4	0.63	Mod. rapid
Br1 lower	0.4-0.5	30	58.6	7.3	49.7	3.4	1.4	0.63	Mod. rapid
Br2 upper	0.5-0.6	29	59.1	8.4	49.4	Dis ^B	0.11	0.08	Moderate
Br2 lower	0.6-0.7	29	57.6	1.8	54.7	Dis ^B	0.11	0.08	Moderate
2Bg	0.7-0.8	55	60.7	2.2	58.0	0.1	0.03	0.07	Slow
2Brx	0.8-1.0	60	58.1	0.5	57.3	0.01	0.02	0.02	Very slow
3Cr	1.0-1.1	7	48.7	8.4	40.0	0.0	0.05	0.22	Mod. slow
4Cr	1.1-1.2+	7	48.5	20.7	18.0	315.6	0.23	0.22	Rapid

^A See Clayden and Hewitt (1989)^B Dispersed on saturation

9.4 Models

9.4.1 DRAINMOD

DRAINMOD (Skaggs, 1980a, 1980b) is based on a water balance in the soil profile midway between parallel subsurface drains. The model was developed specifically for soils with shallow water tables (Skaggs 1980a), and is now the mostly widely used model for water table management in the USA (Desmond *et al.*, 1996). Approximate methods are used to quantify the hydrological components such as subsurface drainage (Hooghoudt and Kirkham equation) and infiltration (Green and Ampt equation). The model considers that soil evaporation and plant transpiration requirements are one evapotranspiration demand. This demand is met initially from upward flux from the water table. If this upward flux can not satisfy this demand then soil water depletion from the rooting zones occurs. This soil water extraction occurs down to the water content at wilting point. If these two supply mechanisms still cannot satisfy the potential demand then evapotranspiration is considered to be limited for that day. As discussed earlier, complex numerical methods are avoided in the soil water distribution method by using a lookup table which relates the air-filled porosity or drainage volume in the soil profile to the height of the water table. In the unsaturated zone a 1:1 relationship between matric potential and distance from the water table is assumed (Skaggs, 1980b). DRAINMOD uses hourly rainfall data. Simulation time steps vary from 1 day, when no rainfall or irrigation occurs and drainage outflow is low, down to hourly time steps, when rainfall and/or surface ponding conditions exist.

Interlayer fluxes can be calculated by DRAINMOD (Skaggs *et al.*, 1991) by dividing the unsaturated zone into a number of increments or layers. Starting with the known flow into the water table, the change in the soil water content in the layer immediately above the water table is calculated for the given time period. The flux into the upper layer is then deduced as the flow required to produce this change in soil water

storage and the outflow from the layer going into the water table. To estimate the inter-layer fluxes throughout the profile this procedure is then repeated sequentially for all layers up to the soil surface.

As provisions for controlled drainage systems are included in DRAINMOD, only minor modifications to the source code were required to simulate the controlled water table regime used in the lysimeters. When the water table height was below that of the weir in the outlet tube, the drainage outflow was set to zero. When the predicted water table height exceeded that of the weir, the drainage volume was calculated as the quantity necessary to reduce the water table height back to the height of the weir. The computational time step was set to 1 hour regardless of soil surface conditions.

9.4.2 *SWIM*

A modified version of the CSIRO hydrology model SWIM (Soil Water Infiltration and Movement) was also used (Ross, 1990a) to simulate the soil water conditions in the lysimeters. SWIM is based on the mass-conserving mixed form of Richards' equation using a fixed spatial grid and hyperbolic sine transform for the soil matrix potential. The solution method is based on applying the Thomas algorithm to find the solution of a Jacobian matrix when applying the Newton-Raphson numerical approximation (Ross, 1990b). SWIM uses a more complex plant water uptake algorithm than DRAINMOD. The water flux to the roots is determined as a function of xylem potential, root properties, and soil water characteristics.

To simulate weir-type controlled drainage, the source code was altered to adjust the tension (ψ) state vector and water content (θ) whenever ψ in the last or bottom layer of the simulated profile indicated that the water table height had reached the height of the weir. The ψ value for a layer i within the water table was calculated on the basis of hydrostatics as the distance from the top of the water table to layer i . The ψ value for a layer i above the weir was estimated by subtracting the "overshoot" (weir height minus unmodified ψ in the bottom layer) from the unmodified $\psi(i)$. The saturated zone rises only during wet conditions, during which the ψ distribution follows an "equilibrium" pattern with a one to one relationship to vertical depth (dz). Therefore, the modification described should produce realistic drainage values. To avoid an excessive overshoot of the weir height in one iteration, SWIM's original time step was divided by 2-16 times as the water table height approached the weir height. From a base time step (dt) of 15 minutes the minimum dt , used during wet periods, was approximately 1 minute.

9.4.3 *Input parameters for DRAINMOD and SWIM*

The input parameters and method of determination used to run DRAINMOD and SWIM for the three different drainage conditions (conventional, controlled-low, and controlled-high) are summarised in Tables 9.5 and 9.6. The data requirements for both models are quite similar and in all cases parameters were derived from the same data sets.

Table 9.5 Input parameters used for DRAINMOD.

Parameter	Value or data table	Source or method of determination
Wilting point	0.27 m ³ m ⁻³	Measured average soil water content at 1500 kPa matric potential for topsoils
Rooting depth	0.15 m	Estimated 60% value for ryegrass-clover pasture
Soil water versus matric potential	By horizon	Measured on 54 mm dia. by 30 mm undisturbed cores using the method of Gradwell and Birrell (1979)
Water table height versus volume drained	By depth	Derived from soil water versus matric potential for 9 horizons using the method WTVOLDRN (Skaggs, 1980a)
Drainage configuration	Not used	DRAINMOD was modified to determine lysimeter drainage independent of the physical drainage configuration i.e. spacing etc.
Unsaturated hydraulic conductivity	By horizon	Combination of measured data using suction permeameters on soil core (98 mm dia. by 70 mm) using the method of Millington and Quirk (1960)
Upward flux versus water table height	By depth	Calculated from unsaturated hydraulic conductivity data using the method of Skaggs (1980a)
Soil infiltration rate	By depth	Green and Ampt parameters determined from measured water content versus soil matric potential data and estimated unsaturated hydraulic conductivity

Table 9.6 **Input parameters used for SWIM.**

Parameter	Value or data table	Source or method of determination
Grid spacing	0.01 m for top 0.03 m 0.02 m down to 0.05 m 0.05 m to 1.2 m	
Minimum xylem	1500 kPa	Estimated soil matric potential at wilting point
Rooting depth constant	0.09 m	Depth when rooting density falls to 37% estimated from Haynes and Francis (1993)
Maximum root length density	5.5 m ³ m ⁻³	Data for ryegrass and clover from Haynes and Francis (1993)
Vegetation PET fraction	1.0	Permanent pasture leaf area index considered to be greater than 2.7 over entire year
Saturated moisture content	By horizon	Measured on undisturbed cores (54 mm dia. by 30 mm) using the method of Ball and Hunter (1988)
Soil hydraulic properties	By horizon	Derived from measured soil water versus tension data (Gradwell and Birrell, 1979) using the method of Hutson and Cass (1987)
Saturated hydraulic conductivity	By horizon	Measured data using suction permeameters on undisturbed cores (98 mm dia. by 70 mm)
Soil surface storage	0.05 m	Measured
Surface conductance	0.048 m h ⁻¹	Based on soil surface infiltration rates

9.5 Results and discussion

9.5.1 Drainage

The predicted and measured drainage on an annual basis is given in Table 9.7. The standard error of deviation per daily measurement, calculated from Equation (9.1), and the ratio of actual to predicted drainage for each treatment are also given. It should be remembered that in this work both models are not calibrated, i.e. model parameters have not been fitted or adjusted to improve the predictions made.

On an annual basis, both models gave excellent estimations of the total amount of drainage that occurred across all treatments. The predicted cumulative drainage over the 4 years of data varied between 0.93 and 1.16 of the measured values. In all of the treatments DRAINMOD tended to over-estimate the annual drainage (mean measured/predicted = 0.95), whereas SWIM tended to under-estimate (mean measured/predicted = 1.10).

As others have found (Evans *et al.*, 1991; Skaggs *et al.*, 1995; Drury *et al.*, 1996), measured subsurface drainage volumes decreased with increasing water table control height. The same relationship was also observed in this study, although the trend could not be shown to be statistically significant. Under field

conditions, the lower drainage volumes are a function of increased deep seepage losses due to the higher hydraulic head, as well as higher evapotranspiration losses due to wetter soil conditions. As the lysimeters were constructed with an impermeable base, seepage losses could not increase with the higher hydraulic head (as created with higher controlled drainage heights), so the only mechanism for decreasing drainage on the lysimeters was greater evapotranspiration. Both models were capable of predicting the trend of decreased drainage with increasing water table height (Table 9.7). SWIM over-predicted the difference in drainage between the conventionally drained treatment and the highest water table treatment (0.5 m weir height) as 580 mm compared to the measured value of 190 mm, whereas DRAINMOD predicted the span well at 220 mm.

Table 9.7 Comparison of predicted and measured drainage for the three drainage treatments. Data shown for 1992 and 1996 are for the last and first 6-months respectively; the first 2 replicates ran for only 2-months in 1996. Target mean is an adjusted mean accounting for some data exclusion due to equipment failure. Replicate variation is the drainage depth variation about the mean; as data for the final 4-months of 1996 comprised only 1 replicate variation, data for this period are not available. Error is the standard error of deviation; ratio is measured/predicted values. All data synchronised with drainage collections.

Year	Target mean (mm)	Replicate variation		DRAINMOD			SWIM		
		Plus (%)	Minus (%)	Depth (mm)	Error (mm)	Ratio	Depth (mm)	Error (mm)	Ratio
Conventional drainage treatment									
1992	616	5.9	5.7	649	5.4	0.95	668	6.0	0.92
1993	562	9.9	8.2	672	3.2	0.84	664	2.9	0.85
1994	923	2.4	3.5	885	2.9	1.04	870	2.8	1.06
1995	1341	2.3	3.8	1390	3.9	0.96	1280	3.2	1.05
1996	355	-	-	371	4.1	0.96	295	4.0	1.20
1992-96	3797	4.5	2.9	3967	3.6	0.96	3777	3.4	1.01
Controlled-low drainage treatment									
1992	569	11.4	6.1	649	5.2	0.88	572	5.5	0.99
1993	498	3.3	3.1	672	3.3	0.74	526	2.2	0.95
1994	894	2.8	2.1	885	2.6	1.01	731	2.5	1.22
1995	1373	1.9	3.6	1380	3.9	0.99	1186	3.6	1.16
1996	334	-	-	367	4.0	0.91	237	4.8	1.41
1992-96	3668	0.6	0.4	3953	3.6	0.93	3252	3.4	1.13
Controlled-high drainage treatment									
1992	580	5.9	4.9	605	4.8	0.96	558	4.2	1.04
1993	532	8.6	13.0	643	3.2	0.83	504	2.5	1.06
1994	893	5.3	4.4	847	2.7	1.05	719	2.6	1.24
1995	1279	3.6	2.7	1319	3.8	0.97	1154	3.4	1.11
1996	367	-	-	309	3.4	1.19	222	5.4	1.65
1992-96	3651	4.9	4.6	3723	3.4	0.98	3157	3.4	1.16

The drainage predictions by both models in this study were better than those reported in previous field studies (Table 9.1). This improved performance may have been a function of the essentially 1-dimensional nature of the lysimeters' hydrology, with the absence of lateral fluxes. In this study, the prediction of drainage was based solely on the height of the water table and did not require a quasi 2-dimensional approach to incorporate drainage fluxes and drain configuration as used in other studies. The retention, by the lysimeter casing, and subsequent infiltration of any ponded water also eliminated runoff as another potential source of error.

The residual plot with time (Figure 9.2) shows little bias, although there is a slight predominance of positive errors (DRAINMOD) and negative errors (SWIM) as would be expected from the total drainage values. Generally the greatest errors in drainage are associated with rain events over summer and autumn. During these periods the soil is at its driest. There are long intervals, up to 8 weeks, when drainage does not occur. As the predicted ET rates at this time are less than the potential rates (PET), any errors in simulating a limited ET rate would manifest themselves at this time. Therefore these periods are opportunities for the simulated soil moisture condition to deviate significantly from the actual condition without any error revealing itself in drainage fluxes or water table heights. Any accumulated error becomes apparent only when a significant rain event causes drainage. It should be noted that differences between replicate lysimeters are also greatest during these wetting-up events.

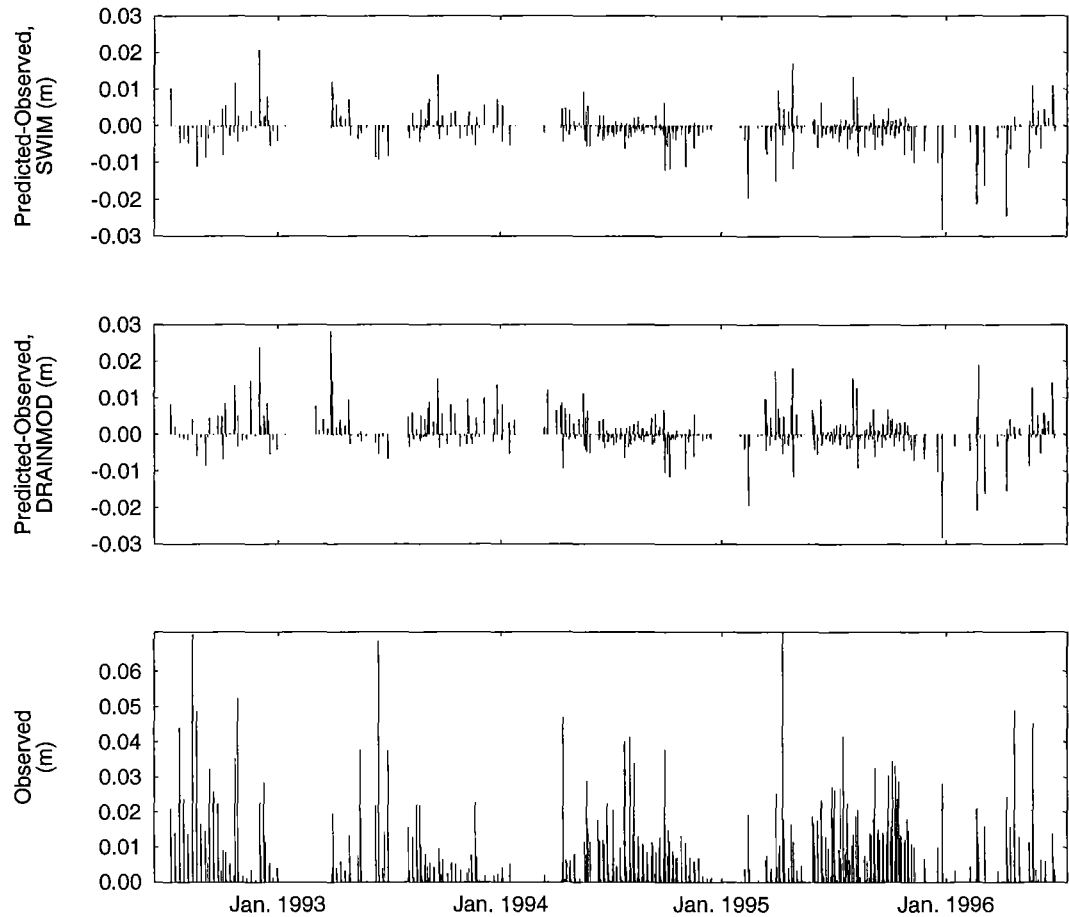


Figure 9.2 Residual plot of (predicted - measured) drainage values, for the controlled-low drainage treatment for both DRAINMOD and SWIM over a 4-year period.

To compare performance between the models, the residuals (predicted-measured) generated by each model for the controlled-low treatment are plotted against each other (Figure 9.3a). Both models tend to show the same consistency in the residuals (i.e. both over or both under). This is evident from the data points being predominantly in Quadrants 2 and 4. When SWIM over-estimated a value, DRAINMOD's corresponding estimation tended to be even higher, as most data points in Quadrant 2 are above the 1:1 line. When SWIM under-estimated a drainage volume then the corresponding DRAINMOD residual error tended to be smaller. This result is consistent with DRAINMOD tending to over-estimate drainage volumes and SWIM to under-estimate them. There were more instances of SWIM under-estimating a drainage volume with a corresponding DRAINMOD over-estimation (Quadrant 1) than the converse of DRAINMOD under-estimating coupled to a SWIM over-estimation (Quadrant 3).

When the residuals from the models are compared with the size of the measured event (Figure 9.3b), it is obvious that it is not the larger sized events which generated the larger residuals. As discussed above, the larger residuals are associated with the time of the event rather than the size of the event. It was drainage fluxes from rainfall events over summer and autumn which proved to be the most difficult for both models to predict.

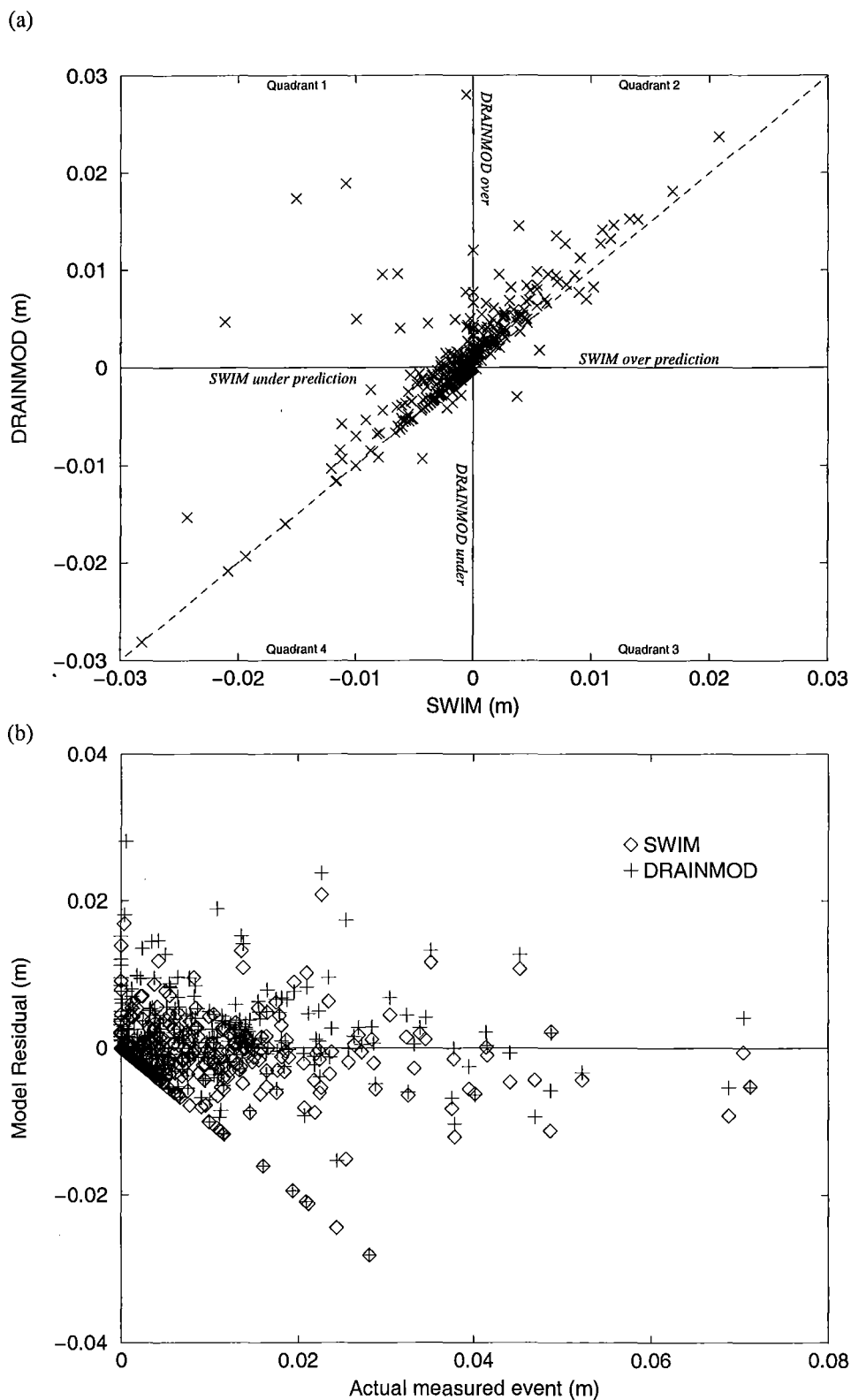


Figure 9.3 (a) Residual plot of (predicted - measured) drainage values from DRAINMOD versus the same residual data from SWIM, for the controlled-low drainage treatment. (b) Residual plot from SWIM and DRAINMOD for the controlled-low drainage treatment versus size of the measured event.

9.5.2 Water table heights

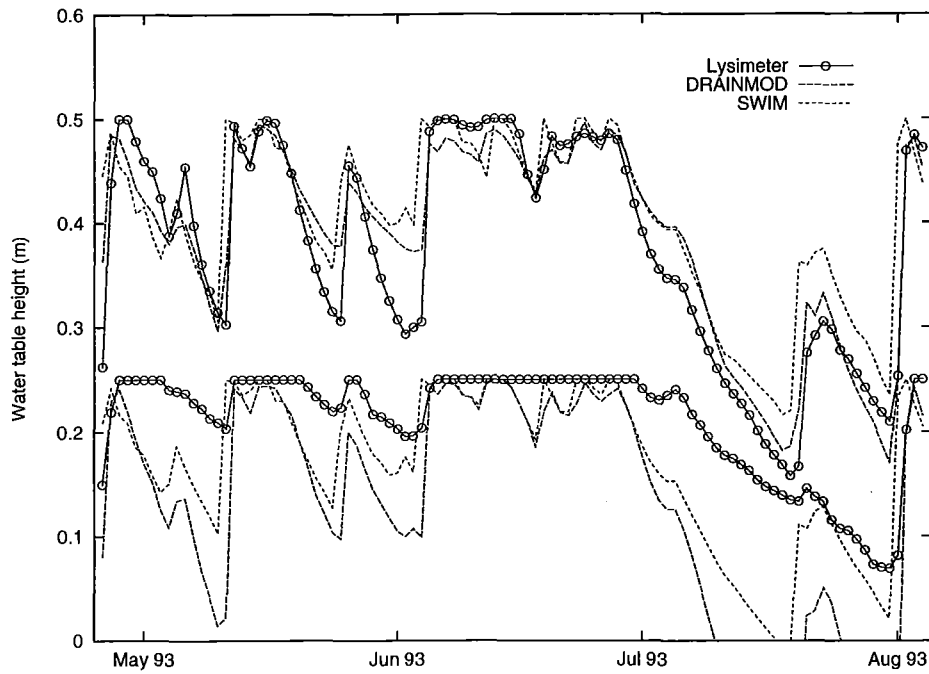
The standard errors in the prediction of the daily water table heights by both models are given in Table 9.8. While the measured water table height was available on a 3-hourly interval, this was not used because DRAINMOD calculates water table height on a daily basis. For both models, the standard errors associated with the prediction of the water table heights are approximately half those of field studies shown in Table 9.1. As discussed previously, the 1-dimensional nature of lysimeters, and the elimination of surface runoff, probably contributed to the lower standard errors in this study. Also, the controlled drainage installed in these lysimeters limited the maximum height of the saturated zone and consequently reduced the possible magnitude of the error. This limiting of standard error is also relevant to comparisons made between the two controlled drainage treatments.

Table 9.8 **Number of measurements and standard error of daily water table heights for controlled drainage treatments.**

Year	Number of measurements	Controlled-low		Number of measurements	Controlled-high	
		DRAINMOD	SWIM		DRAINMOD	SWIM
1992	151	0.10	0.06	151	0.09	0.06
1993	365	0.10	0.08	365	0.09	0.11
1994	350	0.09	0.08	353	0.10	0.09
1995	355	0.11	0.07	357	0.17	0.09
1996	65	0.11	0.06	182	0.21	0.12
1992-96	1286	0.10	0.07	1408	0.14	0.10

As demonstrated by the low standard errors, both models did very well in predicting the height of the water tables. The standard errors of the water table height predicted by SWIM are generally lower than those associated with DRAINMOD. As can be seen in Figure 9.4a, SWIM does tend to track the measured values more closely than DRAINMOD. It is also evident from Figure 9.4b that for the controlled-low treatment, both models predicted more extraction than what was actually measured. The controlled-high treatment also over-estimated extraction, although to a lesser degree; model fluctuations agreed more closely with those measured. The same plant rooting depth information and potential evapotranspiration data were used for all drainage treatments. Any plant adaption to water table conditions, or differences in soil evaporation behaviour and resulting difference to the extraction profile, could account for the observed deviation.

(a)



(b)

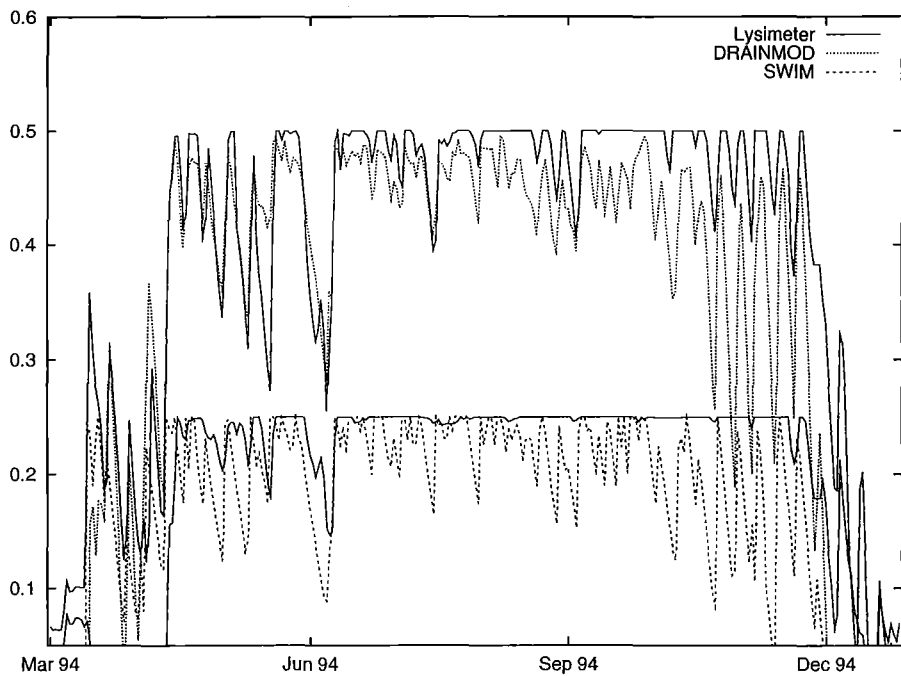


Figure 9.4 (a) Water table predicted versus measured for controlled-high (upper lines) and controlled-low (lower lines) drainage treatments. (b) Overview of long term data, DRAINMOD versus measured for controlled-high, and SWIM versus measured for controlled-low. Lysimeter data are an average of 3 replicates.

9.6 Conclusions

Both water table height and drainage were accurately modelled by DRAINMOD and SWIM, with no obvious superiority between the two models. Therefore, in situations where only daily water table heights and drainage depths are required, and the assumptions inherent in DRAINMOD are generally valid, the simpler DRAINMOD model is preferable. When soil moisture data and inter-layer fluxes are required at smaller time steps, SWIM's more mechanistic approach offers more flexibility. SWIM may also be preferable in dry climatic conditions with low permeability soils, which do not favour the lookup table approach to locate the water table with the "equilibrium assumption" in the unsaturated region. However, without program source modification, only DRAINMOD attempts to incorporate the effects of artificial field drainage configuration, so this may be a dominant factor in model selection.

Whereas DRAINMOD's hydrological performance has been assessed by many authors previously, SWIM has received less verification under high water table conditions. The present study suggests that SWIM has the robustness required to handle an artificially controlled water table scenario. In fact both models handle this drainage configuration well, lending weight to the general validity of their formulation.

9.7 References

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Chapter Ten

CaNS-Eff: A Carbon and Nitrogen Simulation model capable of describing the fate of Dairy Farm Effluent applied onto the land

The objective of this Chapter is to:

Provide a detailed description of CaNS-Eff, a model capable of describing the fate of C and N in organic effluents applied onto the land. Components of the model, the linkages between the components, and the operation of the model are discussed

10.1 Overview of the processes in CaNS-Eff

The schematic of the processes considered in CaNS-Eff both within a layer and between layers is given in Figure 10.1. For simplicity of description, only one layer is shown in detail, but the model is implemented for a multi-layer configuration.

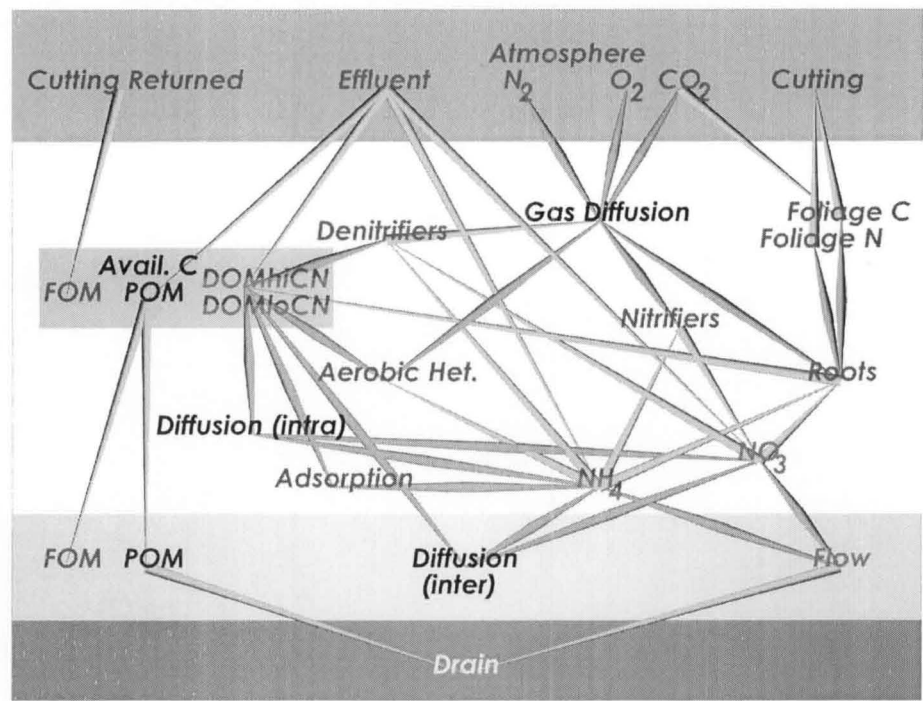


Figure 10.1 Schematic of processes and inputs considered within CaNS-Eff.

Legend for Figure 10.1

NH ₄	Ammonium
NO ₃	Nitrate
Microbial biomass	Aerobic <i>Heterotrophs</i>
	<i>Denitrifiers</i>
	<i>Nitrifiers</i>
Avail. C	Sources of microbially available carbon
- FOM	Fixed organic matter, e.g. <i>native soil organic matter</i>
- POM	Particulate organic matter, e.g. <i>particulate DFE fraction</i>
- DOMhiCN	Dissolved OM high C:N, e.g. <i>dissolved DFE OM high C:N</i>
- DOMloCN	Dissolved OM low C:N, e.g. <i>dissolved DFE OM low C:N</i>
Atmosphere	N ₂ Nitrogen gas in atmosphere
	O ₂ Oxygen gas in atmosphere
	CO ₂ Carbon dioxide gas in atmosphere
Foliage	C Carbon component of foliage
	N Nitrogen component of foliage
Roots	Below-ground component of pasture (C and N both specified)
Effluent	DFE
Cutting returned	Foliage that is cut and returned
Cutting	Removal of foliage by cutting
Gas diffusion	Process of movement of atmospheric gases through the profile
Diffusion (intra)	Dissolved pools move between meso & micropores within layer
Adsorption	Adsorption of selected dissolved components onto soil
Flow	Water and solute movement between layers
Diffusion (inter)	Dissolved pools moved in meso & micropores between layers
Drain	Drain layer in the profile

10.1.1 Processes considered in CaNS-Eff

Table 10.1 summarises the processes and inputs in CaNS-Eff.

Table 10.1 Summary of processes and inputs in CaNS-Eff.

Plant processes	Microbial processes	Transport	Inputs
Foliage growth	Biomass growth and death for 3 popns.	Convective flow in mesopore domain	Dissolved C and N fractions of effluent
Root growth	Nitrification	Mixing (dispersion) in mesopore domain	Particulate C and N fractions of effluent
Rhizodeposition	Denitrification	Intra- and inter-layer diffusion	Returned foliage cuttings
Root death	O ₂ consumption and CO ₂ production by <i>heterotrophs & denitrifiers</i>	Particulate filtration	
Foliage cutting & die off	Ammonification	Transport of O ₂ , N ₂ , and CO ₂	
Translocation of C&N between roots & foliage		Adsorption of NH ₄ , DOM _{high} CN and DOM _{low} CN in mesopore and micropore domains	
Plant uptake of NH ₄ and NO ₃			
Root CO ₂ production			

10.2 Components within CaNS-Eff

CaNS-Eff has been written in C++ and the object-oriented hierarchical class of this language is reflected in the implementation of the components in the model.

10.2.1 Organic classes

All materials within the soil-plant-microbial system that comprise both C and N are implemented as a general CNpool. This general CNpool is split into five classes (Table 10.2) using six criteria (Table 10.3) that reflect how that organic material behaves, moves or interacts within the soil-plant-microbial system. A class is not a unique compound but rather a set of criteria that all pools within that class must obey.

Table 10.2 **Classes of the general CNpool.**

Name of class	Acronym for class	Example of pool within class	Typical C:N	Movable (Transport model)	Microbially available	Size class	Adsorption	Location
Fixed organic matter	FOM	<i>Native soil organic matter</i>	14	No	Yes	Particulate	Non	Whole domain
Particulate organic matter	POM	<i>Particulate fraction of DFE</i>	15	Filtration	Yes	Particulate	Non	Whole domain
Dissolved organic matter high C:N ratio	DOMhighCN	<i>Dissolved DFE OM high C:N</i>	30-60	Soluble	Yes	Dissolved	Isothermic	Split between micropore & mesopore
Dissolved organic matter low C:N ratio	DOMlowCN	<i>Dissolved DFE OM low C:N</i>	6.5	Soluble	Yes	Dissolved	Isothermic	Split between micropore & mesopore
Biomass	BIO	<i>Denitrifiers</i>	7	No	No*	Particulate	Non	Whole domain

* Dead biomass moves into the FOM pool which is a microbially available pool.

Table 10.3 Criteria for describing the classes of the general CNpool.

Criteria	Number of options	Options
Movable	3	Fixed, not movable Movable with the filtration model Movable in solution
Location	2	Not split but exists in the total domain Split into micropore and mesopore domains
Size	2	Dissolved (< 0.2 µm) Particulate (> 0.2 µm)
C:N ratio	Variable	Differentiated on the basis of C:N ratio
Adsorption	2	Isothermic behaviour Non-isothermic behaviour
Microbial availability	2	Available for microbial consumption Unavailable for microbial consumption

10.2.2 *Organic material pools*

There are thirteen organic pools (Table 10.4), of which eight are microbial substrates. A pool is the masses of C and N within a layer over 1m² of area. If the pool is microbially available it will also have an associated availability structure.

Table 10.4 Organic pools simulated in CaNS-Eff.

Class	Pools	Microbially available
FOM		
	<i>Native soil organic matter</i>	Yes
	<i>Dead microbial biomass</i>	Yes
	<i>Dead foliage biomass</i>	Yes
	<i>Dead root biomass</i>	Yes
POM		
	<i>Particulate DFE fraction</i> (seven size-classes)	Yes
DOMhighCN		
	<i>Root exudates</i>	Yes
	<i>Dissolved DFE OM high C:N</i>	Yes
DOMlowCN		
	<i>Dissolved DFE OM low C:N</i>	Yes
BIO		
	<i>Heterotrophs</i>	No
	<i>Nitrifiers</i> (autotrophs)	No
	<i>Denitrifiers</i> (special case of heterotrophs)	No
	<i>Foliage biomass</i>	No
	<i>Root biomass</i>	No

To adequately describe its transport, the *particulate DFE fraction* is divided into seven physical size-classes.

10.2.3 Microbial availability of organic material

The use of first-order kinetics has been found to describe experimental data on the decomposition of plant material reasonably well (Paul and Clark, 1989). The first-order rate equation assumes that the change in mass over time is constantly proportional to the mass (Equation 10.1):

$$\frac{dM}{dt} = -kM \tag{10.1}$$

where:

- M = mass (g m⁻²)
- t = time (day)
- k = decay constant (day⁻¹).

The decay constant reflects how the material is degraded under optimum conditions. Decay constants can be fitted to experimental data to describe the degradation of complex materials such as microbial biomass. Alternatively, as used in CaNS-Eff, the decay constants are characteristics of the different chemical components making up the material undergoing decomposition, e.g. hemi-cellulose, lignin etc. The availability structure of each of the microbially available pools in CaNS-Eff is made up of a number of user-defined bins, each with an associated first-order decay constant describing its availability. Currently, there are nine bins within an availability structure ranging from highly available C substrate (i.e. glucose) to effectively inert organic material. The availability structure also specifies the percentage of the total carbon and nitrogen mass which is contained in each bin. This approach, called multiple availability bins, gives flexibility to describe the degradation dynamics and changing availability with time as outlined in the following section.

One advantage of this approach is that the microbial availability of any material entering the soil system can be described in detail based on the specific chemical composition of the material. For example: *dead microbial biomass* has an availability structure made up of soluble C, cellulose, hemi-cellulose, and lignin. If 12.3 g C and 2.8 g N of *dead microbial biomass* existed in a soil layer and it was assumed to be made up of 40% soluble C, 25% cellulose, 20% hemi-cellulose and 15% lignin, this would have an availability structure as given in Table 10.5.

Table 10.5 Example of availability structure of *dead microbial biomass*, showing percentage in each availability bin.

C g m ⁻²	N g m ⁻²	Soluble C (%)	Cellulose (%)	Hemi-cellulose (%)	Lignin (%)
12.3	2.8	40.0	25.0	20.0	15.0

This structure also allows materials of differing availability to be added or subtracted together. For example, *dead microbial biomass* which is considered to be in the FOM class (i.e. non-movable, and

microbially available) can be added to the *native soil organic matter*, also in the FOM class. The resulting availability structure from the addition of the two pools reflects the combined availability based on prorating of the carbon amounts. An example is shown in Table 10.6.

Table 10.6 **Example of adding dead microbial biomass to the native soil organic matter pool, firstly showing the availability spectrum on a percentage basis and secondly on a g m⁻² basis.**

	C	N	Soluble C	Cellulose C	Hemi-cellulose C	Lignin C	Waxes & fatty acids	Stabilised organic matter
	g m ⁻²	g m ⁻²	(%)	(%)	(%)	(%)	(%)	(%)
<i>Native soil organic matter</i>	1100	92	0.0	5.0	5.0	10.0	35.0	45.0
<i>Dead microbial biomass</i>	12.3	2.8	40.0	25.0	20.0	15.0	0.0	0.0
Resultant native soil organic matter	1112.3	94.8	0.4	5.2	5.2	10.1	34.6	44.5
	C	N	Soluble C	Cellulose C	Hemi-cellulose C	Lignin C	Waxes & fatty acids	Stabilised organic matter
	g m ⁻²	g m ⁻²	g m ⁻²	g m ⁻²	g m ⁻²	g m ⁻²	g m ⁻²	g m ⁻²
<i>Native soil organic matter</i>	1100	92	0.0	55.0	55.0	110.0	385.0	495.0
<i>Dead microbial biomass</i>	12.3	2.8	4.9	3.1	2.5	1.9	0	0.0
Resultant native soil organic matter	1112.3	94.8	4.9	58.1	57.5	111.9	385.0	495.0

The availability structure of a pool will also change with time. As the more available fractions of the pool are used, the percentages of C remaining in the more available bins will decrease and the percentages in the less available bins will increase. All of the C that is considered to be microbially available may not be used in a single time step, as the uptake kinetics or the demand of the biomass may be less than the microbially available C.

10.2.4 Inorganic pools

Apart from the organic N pools there are two inorganic N pools, ammonium and nitrate. Oxygen (O₂), dinitrogen (N₂) and carbon dioxide (CO₂) in the soil atmosphere are also state variables.

10.3 Solution to competition for substrates

10.3.1 Substrate competition

A number of microbial and plant processes compete for the same substrate, as summarised in Table 10.7. The general procedure for the solution to this competition is outlined in the following section. Substrate specific details are discussed for O₂ in Section 10.3.2, available C in Section 10.4.2, NH₄ in Sections 10.4.8 and 10.5.6 and NO₃ in Sections 10.4.9 and 10.5.6.

Table 10.7 Competitors for various substrates.

Substrate	Competition between
Microbially available C	<i>Heterotrophs, denitrifiers</i>
Nitrate	<i>Root biomass, denitrifiers</i>
Ammonium	<i>Root biomass, heterotrophs, denitrifiers, nitrifiers</i>

The allocation of the available substrate between competitors is based on:

1. the uptake rate at which each of the competitors can compete for the substrate, and
2. the absolute demand for substrate by each competitor.

The procedure to determine a solution to the competition is as follows:

1. The uptake rate for the resource is determined for each of the competitors for the current environmental conditions and assuming no resource limitation.
2. The demand for the substrate by each competitor for that time period is calculated.
3. The uptake rates for all of the competitors are summed into a cumulative uptake rate for the resource.

Each competitor is allocated the smaller of:

- (a) their demand, or
- (b) a fraction of the substrate pro-rated on the basis of uptake rates, i.e.

$$\text{resource} * \frac{\text{uptake rate of this competitor}}{\text{sum of uptake rates for all competitors}}$$

4. The demand of each competitor is decremented by the amount allocated to each competitor.

5. The procedure is repeated for every competitor as long as it has a demand and substrate remains.

Some substrate may remain after the completion of one allocation cycle because a competitor's demand may be less than its maximum uptake rate over the time increment dt . This results in the competitor not requiring all of the substrate that they could potentially acquire through competition and some substrate remains. This remaining substrate is allocated by repeating the procedure for the remaining competitors.

10.3.2 Oxygen allocation to competitors

Oxygen is utilised by four processes in CaNS-Eff: *root biomass* respiration and aerobic activity of the *heterotrophic*, *denitrifier* and *nitrifier* populations. The oxygen in a layer is allocated to the competing processes on a pro-rata basis using one of three options:

1. Amount of biomass-C

This option uses the mass of competitor C present in a layer to distribute the available oxygen.

2. Baseline respiration requirement

This option ignores the current respiration rate and uses the maintenance respiration rate and the size of the microbial biomass to determine a baseline respiration rate. The baseline respiration rate for the *root biomass* is determined from the root respiration rate and the amount of root-C in a layer.

3. Respiration requirement based on allocated resource.

The third option is based on the respiration requirements of the allocated substrates for each competitor. These oxygen demands are summed for the four competitors and the available oxygen pro-rated to each of the competitors based on their individual demands as a percentage of the sum.

10.4 Microbial dynamics

10.4.1 Microbial biomass

The microbial biomass is divided into three different functional populations. The largest of these is the *heterotrophic biomass* which consumes available C and oxygen for respiration and growth under aerobic conditions and uses both organic N and ammonium to maintain an optimum C:N ratio. The second biomass pool, *denitrifiers*, is identical to *heterotrophs* except that they can use nitrate as an alternative electron donor under oxygen-limiting conditions. The third biomass pool, *nitrifiers*, use ammonia as their energy source as well as for CN balancing during growth and produce nitrate from their chemo-autotrophic activity.

10.4.2 Substrate for microbial dynamics

Microbially available C is derived from four different classes (Table 10.8).

Table 10.8 **Classes which contribute to microbially available C.**

Class	Location in profile	Pools which contribute to available C
DOMhighCN (dissolved)	Micropore & mesopore domain	<i>Dissolved DFE OM high C:N, root exudates</i>
DOMlowCN (dissolved)	Micropore & mesopore domain	<i>Dissolved DFE OM low C:N</i>
POM	Whole domain (seven size-classes)	<i>Particulate DFE fraction</i>
FOM	Whole domain	<i>Native soil organic matter, dead microbial biomass, dead root biomass, dead foliage biomass</i>

As microbial biomass exists uniformly through the whole soil profile, the “concentration of available C” in the soil solution is determined using the total amount of water in a layer. If not all of the available C is used in a time step the contribution that each of the sources makes is based on pro-rating the amount used against the potential contributions.

The *nitrifiers* are a special case as their energy is derived from the conversion of NH_4 to NO_3 . In this case the substrate is the dissolved NH_4 as discussed in Section 10.4.10.

10.4.3 Determination of the respiration rate

The biomass populations each have two respiration rates specified: a maintenance rate, which is the minimum respiration rate that occurs when the biomass is dormant, and a second higher growth rate. The biomass respiration will shift towards the growth respiration rate when excess substrate is available. If insufficient substrate is available to maintain the population at the minimum maintenance rate, biomass death will occur and self-consumption is used as a mechanism to maintain the biomass population.

A variable (m_{cs} , carbon seconds) controls the transition between the two respiration rates. The m_{cs} is similar to the degree days concept in plant growth and tracks the time period that the available C is above the maintenance respiration requirement. The amount of excess C on m_{cs} is incorporated into the calculation of m_{cs} . When a large excess of C above the maintenance demand exists, then m_{cs} is incremented by a larger amount than if the excess is only small.

10.4.4 Competition for available C

The *heterotrophs* and *denitrifiers* both require C as an energy source. The microbially available C is allocated to these two microbial populations based on the rate at which a population can uptake C and the demand for C, as discussed in Section 10.4.2.

The uptake rate for C for each biomass population is determined from a Michaelis-Menten expression (Equation 10.2) which includes temperature and C:N ratio effects. Oxygen requirements are not considered at this stage to be limiting as the amount of oxygen required is dependent on the amount of C allocated to the biomass.

$$\text{Carbon Uptake Rate} = \text{Bio_grow_tmp} * \text{Bio_grow_CN} * \left[\frac{V_{\max} * \text{AvailConc}}{K_m + \text{AvailConc}} \right] * \text{Biomass_C} \quad (10.2)$$

where:

Bio_grow_tmp = temperature effect on microbial biomass activity

Bio_grow_CN = C:N effect on microbial biomass activity

V_{\max} = maximum uptake rate of C by a microbial population

AvailConc = microbially available C / total water in the layer

Biomass_C = mass of biomass-C in the layer

K_m = half-saturation constant, i.e. concentration of available C when the uptake rate is at half the maximum rate (V_{\max}).

The inclusion of the C:N effect follows McGill *et al.* (1981) where the uptake of the C from a decomposing C source may be slowed if insufficient N is available for the biomass growth. The microbial C:N ratio is used as an indication of the availability of N in the system.

If the biomass is in a growth phase, the maximum amount of C required in a time step is determined from the uptake rate (Equation 10.2) multiplied by the time period, dt . If growth is not occurring the maximum amount of C required is limited to the smaller of:

- (a) the current respiration demand, or
- (b) the amount of C that can be oxidised given the oxygen allocation to the biomass.

10.4.5 C consumption by microbial biomass

Once the available C has been allocated to the biomass, it must then be determined how the substrate is used. The first step in this process is to determine the achievable respiration of the existing biomass, which is the minimum of:

- (a) oxygen available for respiration, or
- (b) C allocated to the biomass.

When an oxygen limitation occurs, *denitrifiers* can use nitrate as an oxidising agent for C respiration. The use of nitrate in such a manner includes a conversion factor to account for the lower energy efficiency of C utilisation under nitrate reduction compared to O₂ reduction.

Available oxygen (and NO₃ for *denitrifiers*) and C substrate (NH₄ for *nitrifiers*) determines the achievable respiration. This achievable amount is compared to the respiration demand from the existing level of microbial activity. If the microbial respiration demand is more than what could be achieved, microbial death is simulated as discussed in Section 10.4.6. Whether C or O₂ limitation actually caused the respiration shortfall is unknown at this stage. An achievable respiration rate greater than demand indicates surplus substrate and microbial growth may occur, as discussed in Section 10.4.7. Aerobic respiration is simulated by conversion of the appropriate amount of available C into CO₂.

Depending on the C:N ratio of the biomass, the organic N associated with the respired C may either be assimilated into microbial biomass or mineralised as NH₄. Any NH₄ mineralised in the soil is pro-rated into micropore and mesopore domains based on the water volume in each domain. The assimilated biomass-N may be released as NH₄ via the ammonification pathway shortly after incorporation if the C:N ratio of the biomass falls below the optimum value.

10.4.6 Microbial death

An achievable respiration rate lower than the demand rate may be due to two mechanisms. Firstly, the amount of C allocated is not sufficient to permit the existing biomass to sustain the current respiration level. Alternatively, the amount of oxygen available for aerobic respiration may be insufficient to oxidise the C necessary to meet the demand. The response of the microbial biomass population differs depending on the reason for the shortfall.

Microbial death and self-consumption is induced if the shortfall was due to a lack of C. *Dead microbial biomass* is considered to belong to the FOM class with a C availability structure representing dead biomass (Table 10.5). The amount of biomass to kill to meet a shortfall is determined from Equation (10.3):

$$\text{Biokill} = \frac{(\text{respReq} - \text{respAct})}{(\text{bioProxyavailin}(dt) / \text{bioProxy})} \quad (10.3)$$

where:

Biokill = amount of microbial biomass-C to kill off in response to a C substrate shortage

respReq = respiration demand of the existing biomass

respAct = respiration rate that is actually achievable with the allocated C

bioProxyavailin(dt) = microbially available C from dead biomass in a dt period

bioProxy = *dead microbial biomass*.

A check is completed to determine if there is sufficient oxygen (and NO₃ for *denitrifiers*) to oxidise the *dead microbial biomass* C. The oxygen used in consuming this *dead microbial biomass* is the minimum of:

- (a) the remaining oxygen in a soil layer, (initial oxygen - oxygen consumed), or
- (b) the oxygen demand of the C from the *dead microbial biomass*.

If necessary, *denitrifiers* also have the ability to use allocated nitrate to meet an oxygen demand.

The respiration rate of a newly grown microbial biomass population is be maintained at an elevated level, even under C shortfall conditions, to provide a more rapid death of this transient population. To achieve this effect the biomass activity variable (m_cs) is decremented at a slower rate during a period of C shortfall after growth than during growth.

If a respiration shortfall has occurred due to an oxygen shortfall (and NO₃ for *denitrifiers*), biomass death can not provide additional respiration. Death under these conditions is still appropriate as the biomass is under stress. Death under oxygen limiting conditions is simulated by Equation (10.4):

$$\text{Biokill} = \text{anaerobic_death_k_factor} * (\text{respReq} - \text{respAct}) \quad (10.4)$$

where:

Biokill = biomass that dies due to an oxygen shortfall

anaerobic_death_k_factor = constant factor for O₂ shortfall induced death.

10.4.7 Microbial growth

C that has been allocated to microbial biomass and has not been used to meet respiration requirement, is available for microbial growth. The variable that describes the activity status of the biomass (m_{cs}) must be exceeded for a specified time period (cs_{grow}) before the biomass can grow. The time delay (cs_{grow}) is the period necessary for the synthesis of growth enzymes. During this transition period the respiration demand is increased linearly from the maintenance to the growth rate, but no increase in biomass-C occurs.

10.4.8 Competition for ammonium by microbial populations

As described in Section 10.3.1 the solution of competition for substrates requires the uptake rate and the maximum required amount of a substrate to be known. The simulation of ammonium uptake for the three microbial biomass populations uses the same Michaelis-Menten expression, with differing parameters, based on the dissolved ammonium concentration and modified by temperature effects (Equation 10.5)

$$\text{Ammonium Uptake Rate} = \text{Bio_grow_tmp} * \left[\frac{V_{\max} * \text{NH}_4\text{DissConc}}{K_m + \text{NH}_4\text{DissConc}} \right] * \text{Biomass_C} \quad (10.5)$$

where:

Bio_grow_tmp = temperature effect on microbial activity

V_{\max} = maximum uptake rate for ammonium by a microbial population

$\text{NH}_4\text{DissConc}$ = dissolved ammonium concentration / total water in the layer

Biomass_C = biomass-C in the layer

K_m = half saturation constant, i.e. the concentration of dissolved ammonium when the NH_4 uptake rate is at half the maximum rate (V_{\max}).

The maximum amount of ammonium required over the time period, dt , is the minimum of:

- (a) the uptake rate (Equation 10.5) over the time period dt , or
- (b) the NH_4 required to return the microbial biomass population back to the optimum C:N ratio.

The ammonium that has been allocated to *heterotrophs* and *denitrifiers* is immobilised. *Nitrifiers* use the ammonium as an energy source, converting it to nitrate as discussed in Section 10.4.10.

10.4.9 Nitrate uptake by denitrifiers

Denitrifiers and *root biomass* are both capable of using nitrate. The *denitrifiers* will however only use nitrate if insufficient oxygen is available for oxidising their allocated C. Nitrate is allocated between *root biomass* and *denitrifiers* using the competition algorithm as discussed in Section 10.3.1. The nitrate uptake rate by *denitrifiers* is a similar Michaelis-Menten expression to Equation 10.5 except that the parameters and concentrations refer to nitrate as opposed to ammonium. A C:N modifying factor is included to account for microbial efficiency varying as the biomass shifts away from the optimal C:N ratio.

As oxygen consumption occurs with C oxidation it is difficult to pre-determine when an oxygen shortfall will occur and therefore when *denitrifiers* will require nitrate to oxidise the C. To overcome this problem, *denitrifiers* will always compete for nitrate regardless of the oxygen status. Subsequently, if an oxygen shortfall occurs their allocated nitrate can be used as the alternative source for oxidation of their allocated C. If however sufficient oxygen is available, the nitrate allocated to the *denitrifiers* will be passed to the plants provided they have a demand for it. The nitrate-N that is used for C oxidation by the *denitrifiers* is converted to N_2 gas.

The nitrate that can be converted to N_2 gas by the *denitrifiers* is the minimum of:

- (a) nitrate allocated to the *denitrifiers*, or
- (b) any respiration requirement that is not met by aerobic oxidation, or
- (c) any allocated C that has not been oxidised under aerobic conditions.

10.4.10 Nitrification

Nitrifiers have no organic C requirement for maintenance and growth, as their energy comes from the nitrification (oxidation) of NH_4 to NO_3 and not from C. The *nitrifiers* use CO_2 as their C source for any biomass-C growth that may occur. As in the case of the other two populations, growth may occur if the allocated substrate allows a respiration rate greater than the current respiration demand. There are certain limitations however on how this growth may be achieved for *nitrifiers*. Death of *nitrifiers* will occur if the NH_4 substrate is not sufficient to meet the demands of the existing biomass.

The procedure is thus:

1. *nitrifiers* compete for NH_4
2. the maximum respiration demand that this NH_4 can satisfy is determined from the smaller of:
 - (a) the ammonium allocated, or
 - (b) the respiration demand.
3. The N allocated is decremented by the respiration demand to give the ammonia remaining.

No remaining NH_4 indicates that the respiration demand was not met and *nitrifiers* are substrate limited, requiring death (Equation 10.4). In this situation, *nitrifiers* are considered capable of cryptic or self-consuming growth to sustain their population.

If excess NH_4 exists, both immobilisation and nitrification processes must be simulated concurrently. A growth component ΔC is calculated, which is based on the following rules:

1. The C:N ratio must be balanced for any biomass growth that occurs (if the biomass-N is already high none of the surplus is required for this function)
2. Any surplus NH_4 not required for C:N balancing goes to nitrification.

Mathematically these two rules may be written as:

$$\Delta N = \Delta C * e + \frac{\Delta C + C_0}{\alpha} - N_0 \quad (10.6)$$

where:

ΔN = amount of N going into nitrification (energy source)

ΔC = increase in *nitrifiers* C

e = energy in NH_4 terms required to grow a unit of *nitrifier* C

C_0 = existing *nitrifiers* C

N_0 = existing *nitrifiers* N

α = optimum C:N ratio of the *nitrifiers*.

The first term on the right hand side ($\Delta C * e$) represents the energy required for an increment of ΔC growth in the *nitrifier* biomass. The second term (quotient) is the amount of N necessary for a balanced C:N ratio of the existing *nitrifier* biomass and a ΔC growth increment. The third term (N_0) is the initial N present in the biomass. Therefore the second term minus the third term is the amount of N required for immobilisation of ΔC biomass growth under a balanced C:N *nitrifier* biomass regime.

The ΔN is known from the amount of N allocated to the *nitrifiers* and not used for respiration, but, as the calculation of the C going into biomass (ΔC) relies on the existing biomass C:N ratio, the determination of the growth component is non-trivial. If the biomass is rich in N, immobilisation of N during growth is zero and all NH_4 allocated above respiration requirements can be nitrified to NO_3 . However, if the *nitrifiers* are in a low N state some of the excess NH_4 must firstly be used to optimise the C:N ratio of the biomass prior to NH_4 being used for nitrification and balanced C:N growth.

The growth component (ΔC) can be determined from re-arranging Equation (10.6) as shown in Equation (10.7):

$$\Delta C = \frac{[(\Delta N + N_0) - (C_0/\alpha)]}{e + [1/\alpha]} \quad (10.7)$$

Oxygen limitation may also prevent sufficient respiration, even though a substrate excess has been calculated. Under this situation, death will still occur using Equation (10.4) and dead *nitrifier* biomass is generated but this death will not overcome the oxygen limitations to allow more respiration.

The same routine that calculates the respiration/growth/death for *heterotrophs* and *denitrifiers* using available C as the energy source is used for *nitrifiers* where the energy is derived from the nitrification of the allocated NH_4 .

10.4.11 Ammonification

The microbial biomass C:N ratios are checked against the optimum values after microbial death and growth have been simulated. If excess microbial N exists the N is expelled as NH_4 . The quantity which is mineralised is the minimum of the:

- (a) excess NH_4 , or
- (b) $1.0\text{E-}3 \cdot dt \cdot (\text{optimum} - \text{actual CN}) \cdot \text{Biomass N}$.

The second expression is an approximation to a first-order, N-limited rate loss dependent on the difference in biomass C:N from the optimum and the size of the biomass pool. The NH_4 mineralised is pro-rated into the micropore and mesopore domains dependent on the amount of water present in each of the domains.

10.4.12 Sequence of processes in simulating microbial dynamics

In a continuous looping system it is somewhat arbitrary to define the order in which processes are completed. However, by isolating a single time step the sequence of processes can be given as follows, but it should be recognised that the procedure is repeated many times over. The order of processes considered for each time step is:

1. Competition for ammonium between plants and the three microbial biomass populations is solved
2. Immobilisation of ammonium for optimisation of the current C:N ratio of the *heterotrophs* and *denitrifiers* is completed
3. Competition for nitrate between *root biomass* and *denitrifiers* is solved
4. Competition for available C in the system *heterotrophs* and *denitrifiers*
5. Calculation of achievable respiration rates, based on available C and NH_4 allocated to the *nitrifiers*
6. The required respiration demand given existing environmental conditions are determined for each biomass population
7. The achievable respiration rate is compared against the demand to determine if death or growth will occur
8. Aerobic respiration is simulated

9. Microbial growth and death as appropriate is completed

10. Ammonification based on optimum C:N ratio of the biomass is simulated.

10.5 Plant dynamics

10.5.1 Plant specification

The pasture is considered to be a ryegrass-clover mixture, divided into above-ground *foliage biomass* and below-ground *root biomass*. Both of these pools are part of the microbially unavailable BIO class and must become part of the FOM class pools, *dead foliage* and *dead root biomass*, before they are microbially available.

The optimum ratio between *foliage biomass* and *root biomass*, as well as maximum, minimum and optimum C:N ratios on a seasonal basis, are all specified for the root and foliage components. The root distribution data are specified through activity tables relating the percentage of *root biomass* C to depth for various growth stages through the year.

10.5.2 Potential growth of foliage

A potential rate of growth of the *foliage biomass* is determined from a relationship used in the model GRASS (Baars and Rollo, 1993). The relationship, derived from experimental data collected in the Waikato region, uses daily solar radiation, daily mean soil temperature at 10 cm depth, soil moisture and the amount of standing biomass to predict the potential daily rate of foliage growth in kg of dry matter (DM) per day. The soil moisture effects are incorporated into a drought index that reduces the rate of growth after a prolonged period of dryness, and also delays recovery after drought conditions. The soil moisture effect is implemented using a “single bucket” soil balance based on available water in the rooting depth. The daily meteorological data for running this component of CaNS-Eff are separate from those used in the hydrological soil water model SWIM, which uses hourly time steps.

To simulate growth of *root biomass* the predicted *foliage biomass* growth rate is multiplied by a seasonal foliage:root ratio. The C fixation for both root and foliage growth is considered to occur in the foliage with the root growth component translocated down to the roots.

10.5.3 N limitation on plant growth

The potential foliage *biomass* C fixation (kg DM day^{-1}) is converted to a potential amount of plant-C that can be fixed in the current time step. For this growth to be achieved, sufficient N in the *foliage biomass* must exist to balance the C growth. The N capacity of the *foliage biomass* is determined by comparing the existing C:N ratio of the foliage with the maximum allowable C:N ratio. If this N capacity is greater than the N required for growth the full potential plant-C fixation is allowed to occur, otherwise C fixation is limited to the amount of N that can be matched by the spare N capacity.

10.5.4 Pasture cutting

An input file specifies dates the *foliage biomass* is cut, and a parameter in the configuration file specifies the amount of *foliage biomass* left after a cutting event. The removed biomass is accumulated into cut foliage. Cutting of the *foliage biomass* results in death of *root biomass* in an effort to re-establish the seasonal optimum foliage:root ratio. If appropriate, the cut foliage can be returned to the topsoil layer as *dead foliage biomass* with an availability structure characteristic of cut foliage.

10.5.5 Die-off of foliage

If the predicted C foliage fixation is negative due to extreme environmental stress, N is scavenged from the fraction of *foliage biomass* transferred into the *dead foliage biomass* pool.

10.5.6 Root biomass

The *root biomass* competes with all three microbial populations for NH_4 and with the *denitrifiers* for NO_3 using the competition algorithm as discussed in Section 10.3.1. The *root biomass* uptake kinetics follow the approach of McGill (1981), using Michaelis-Menten equations based on dissolved N concentrations (Equation 10.8):

$$\text{N_Uptake Rate} = \text{Rt_CN} \cdot \text{Rt_Tm} \cdot \text{Rt_Wr} \cdot \left[\frac{\text{V}_{\text{max}} \cdot \text{NConc}}{\text{K}_m + \text{NConc}} \right] \cdot \text{Rt_C} \quad (10.8)$$

where:

Rt_Tm = temperature effect on plant N uptake kinetics

Rt_CN = C:N effect on plant N uptake activity

Rt_Wr = water content effect on plant N uptake activity

V_{max} = maximum uptake rate of N by root biomass-C

NConc = dissolved N (either NH_4 or NO_3) concentration in the layer / total water in the layer

Rt_C = *root biomass* C in the layer

K_m = half saturation constant, i.e. the concentration of N when the uptake rate of N is half the maximum rate (V_{max}).

Equation (10.8) is parameterised for NO_3 or NH_4 depending on which N species is of interest. In the case of NH_4 , a second set of Michaelis-Menten variables is included to represent the two sites of NH_4 root uptake that have been reported (Fried *et al.*, 1965).

The maximum amount of NH_4 and NO_3 required in a time step must also be specified to solve the competition. In the case of plants, this is determined from the uptake rate (Equation 10.6) times dt .

10.5.7 Root biomass death

Root biomass death is assumed to occur continuously at a first-order rate. This death rate will increase if the optimum ratio between the above- and below-ground plant biomass is disturbed by cutting or die-off.

The *dead root biomass* pool is considered to be in the FOM class with an availability structure for dead root matter. Similarly to the foliage, the N is scavenged from the dying material by allowing the dead material to have a higher C:N ratio than that of the live root biomass.

10.5.8 Clover fixation

Using experimental data from Hoglund and Brock (1987), a relationship was derived to predict the percentage of N fixed by clover from the atmosphere, based on soil nitrate concentration in the root zone and soil moisture conditions (Equation 10.9):

$$\% \text{ of N fixed by clover} = 0.9 - 0.3 * (\text{SMD}/\text{MaxAWC}) - 0.004 * \text{NO}_3_PPM \quad (10.9)$$

where:

SMD = soil moisture deficit (mm)

MaxAWC = maximum water holding capacity (mm)

NO₃_PPM = nitrate concentration (in µg N g⁻¹ soil) in the rooting depth.

The amount of N in the clover is determined from the specified percentage of clover in the pasture, the C:N ratio of the clover and the predicted foliage growth. The N fixed by the clover is added directly into the *root biomass* pool. The user of CaNS-Eff can choose between three options to simulate the effect of clover N fixation on the plant mineral N uptake dynamics:

Option 1. Reduce the maximum amount of NH₄ and NO₃ that is required by the plant by the amount of N that is fixed by the clover. This reduction is done prior to the competition stage.

Option 2. Reduce the NH₄ and NO₃ allocated to the plant by the amount of N fixed by the clover. This is done after the competition stage.

Option 3. Simulate no effect on plant N uptake due to N fixation by clover.

10.5.9 Translocation

As C fixation occurs in the *foliage biomass*, and N uptake occurs in the *root biomass*, it is necessary to simulate the translocation of C and N between the two pools. The cutting of *foliage biomass* and death of *root biomass* can cause the flow of C and N to be in the opposite direction to that normally expected.

C translocation flow is based on the optimum foliage:root ratio provided in tabular format by date. The user specifies maximum daily translocation rates of C and N between foliage and roots in both directions. The C flux is simulated as a quasi first-order rate that is dependent on the size of the donor C pool.

The translocation of N is based on equalising the C:N status in both the roots and foliage around the optimum C:N ratio. The implementation takes into account that the roots and foliage have different optimum values and that the tolerances of the root and the foliage to high or low C:N values may be different. The method ensures that the foliage and roots will both have the same N status relative to their optimum. The rate of N transfer is simulated by first-order kinetics related to this maximum rate, the pool of N available to transfer and the difference in N status for each of the sites.

10.5.10 Root rhizodeposition

Root rhizodeposition, which is considered to be the product of exudates and sloughing from the roots, produces a DOMhighCN class pool, *root exudates*, which is microbially available. The mass of exudates is calculated from the root rhizodeposition rate, the amount of root biomass present in a layer, soil moisture and soil temperature. The N in the exudates is determined from a user-specified C:N ratio. The exudates are split between the micropore and mesopore domains based on the amount of water present in each of these zones.

10.5.11 Root respiration

The conversion of O₂ to CO₂ by root respiration is simulated using a root respiration rate and soil temperature. The production of CO₂ relies on sufficient oxygen in the soil layer having been allocated to the roots from competition between the three microbial biomass populations and the *root biomass* as discussed in Section 10.3.2.

10.5.12 Modification of the growth rate

If actual *foliage biomass* data are available, the predicted rate of foliage growth from the plant growth model can be corrected so that the cumulative sum of the standing biomass over a period of time matches the measured amount.

10.6 Transport

10.6.1 Flow domains

Preferential flow of water containing nutrients and chemicals is often observed in heterogeneous field soils (Heng *et al.*, 1999). To describe this phenomenon, recent mechanistic soil water models have incorporated both mobile (mesopore) and immobile (micropore) flow domains (Figure 10.2). The movement of dissolved material between layers in the conductive flow component is considered to occur only in the mesopore domain. The solute and water infiltrating into the mesopore domain mixes with the water and solutes that are currently in that domain and are available to move down the soil profile with the next flux event. This mixing effectively introduces dispersion into CaNS-Eff.

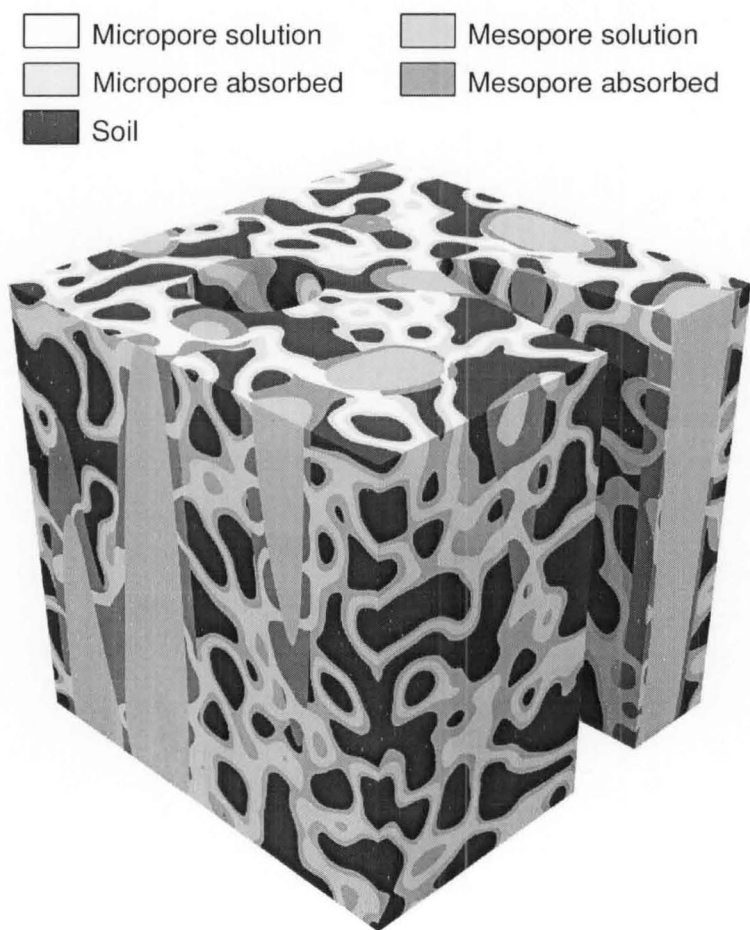


Figure 10.2 Micropore and mesopore domains within the soil profile.

With this implementation, the concentrations of dissolved materials are different in the two flow domains. Diffusion occurs between the micropore and mesopore domains within a soil layer, allowing dissolved material to move into the immobile micropore zone. Diffusion also occurs between the two micropore and two mesopore domains in adjacent soil layers.

The soil matrix can be divided into the two flow domains on the basis of measurements using a disk permeameter (Clothier *et al.*, 1995) or on the basis of a prescribed tension (RZWQM, USDA-ARS, 1992).

As the water content in the mesopore domain decreases, the concentration of solutes in this domain will increase and therefore the net diffusion out of the mesopore domain will also increase. If soil water dries out completely in the mesopore domain, any dissolved material remaining in this domain is transferred into the micropore domain.

Adsorption dynamics, as described in Sections 10.6.3 and 10.6.4, are simulated separately in both domains.

10.6.2 Effluent application

Date and time of effluent application as well as concentration of C and N in the various fractions of the effluent are specified in a user-defined file. The dissolved fractions of the effluent are passed directly into the mesopore domain of soil water when the effluent infiltrates into the topsoil layer. The effluent also contributes to both the *particulate DFE* pool (POM class) and the *native soil organic matter* pool (FOM class) using the particulate filtration model described in Chapter 5. The amount of effluent applied in a time step, dt , is calculated from Equation (10.10):

$$\text{Amount applied} = \text{Conc} * \text{depth} * \frac{dt}{\text{duration}} \quad (10.10)$$

where:

Conc = concentration of the effluent in $\mu\text{g N}$ or C ml^{-1} effluent

depth = depth of effluent applied during the irrigation event (mm)

dt = time step

duration = total time of the irrigation event.

10.6.3 Inter-layer diffusion

Diffusion between layers is considered to occur between adjacent micropore and between adjacent mesopore domains. It is simulated in both directions which allows for any mixing of isotopes or compounds with different microbial availability characteristics.

The amount that diffuses (in one direction) is determined from the dissolved concentration, the diffusion rate, and a tortuosity factor (Equation 10.11):

$$\text{Diffusion} = \frac{\text{Concentration of solute} * \text{Diffusion rate} * \text{Liquid tortuosity factor} * dt}{\text{Distance between layers}} \quad (10.11)$$

where:

Concentration of solute = dissolved concentration of the diffusing material

Diffusion rate = Binary diffusion coefficient of the solute in water

Liquid tortuosity factor = accounts for the increased path length and decreased cross-sectional area of the diffusing solute in soil

Distance between layers = sum of half the thickness of each layer.

The liquid tortuosity factor follows Jury *et al.* (1991), Equation (10.12):

$$\text{Liquid tortuosity} = \frac{(\text{Average water content in both micropore or mesopore domains})^{0.333}}{(\text{Average porosity of micropore or mesopore domains})^{2.0}} \quad (10.12)$$

10.6.4 Intra-layer diffusion

Diffusion from micropore to mesopore domain within a layer is simulated in both directions in a similar manner to that between layers. The tortuosity factor is modified as given in Equation (10.13). It is based on the average water contents, porosities in the layer, and a characteristic distance between the micropore and mesopore domains.

$$\text{Liquid tortuosity} = \frac{(\text{Average water content in the micropore and mesopore domains})^{0.333}}{(\text{Average porosity of micropore and mesopore domains})^{2.0}} \quad (10.13)$$

10.7 Hydrology

CaNS-Eff has been developed for use with separate hydrology models. The information that CaNS-Eff requires is flux between layers and the soil water tension in a layer. CaNS-Eff will interpolate temporal flux events and water contents to resolve this information for the time step required. The spatial information needs to be identical between the hydrology model and CaNS-Eff. Currently the hydrology model used is a modified version of the SWIM model (Ross, 1990).

10.7.1 Adsorption kinetics

The adsorption kinetics used in CaNS-Eff are described in Chapter 6. In summary, CaNS-Eff uses non-equilibrium adsorption kinetics derived from the Langmuir isotherm to describe the adsorption behaviour of NH₄, DOM_{high}CN and DOM_{low}CN. As there are different concentrations of dissolved components in the micropore and mesopore domains, the adsorption kinetics are calculated independently for the two flow domains.

10.7.2 Transport of particulate organic matter

The transport of the particulate organic material ($> 0.2 \mu\text{m}$ in size) in the DFE is presented in Chapter 5. Briefly summarised, the model moves the particulate material from DFE into the topsoil layer, where a proportion of the material is considered to be “trapped” into the *native soil organic matter* pool and thus unavailable for further movement out of the layer. The remaining portion enters the “free” *particulate DFE fraction* in the topsoil layer and may be washed down with further flows. The wash parameter and the size of the water flow control the amount of material that is considered to be “washed out” by a flow event. When this “washed out” material enters the next layer it is again split between the “trapped” *native soil organic matter* and “free” *particulate DFE fraction* pools. The proportion entering the “trapped” pool and the amount moved out of the “free” pool for a given water flow are parameterised for each size-class in the effluent and for each soil horizon considered. Material is not considered to be able to move from one size-class to another.

10.8 Soil atmosphere sub-model

In CaNS-Eff, two sub-models can be used for simulating atmospheric gases in the soil profile. The more simplistic sub-model simulates only oxygen concentration using a lookup table that relates oxygen concentration to soil water tension in a layer. The disadvantage of this approach is that the oxygen level in the soil profile is replenished back to the level specified in the lookup table in subsequent time steps.

The more mechanistic sub-model simulates the gaseous concentration of CO_2 , N_2 and O_2 in the soil profile. The gaseous transport process within the soil profile is done in two steps. The first is the equalisation of pressures where changes in the amount of a gas occur due to:

- changes in pore volume resulting from soil water changes
- changes in atmospheric pressure due to temperature changes
- microbial usage or respiration of gases
- root respiration of CO_2 .

These four factors can cause pressure differences in adjacent layers which require gas to be transferred between layers to maintain an equal atmospheric pressure throughout the soil column. Once pressure equalisation between layers is achieved then the second step of gaseous diffusion is simulated, which allows for molecular equalisation.

10.8.1 Pressure equalisation

The concentrations of O_2 , N_2 and CO_2 throughout the soil column are initially assumed to be at atmospheric concentration and pressure. The volume of a gas in a layer is affected by changes in the pore volume due to soil water movement, as well as temperature effects and concentration changes due to

consumption and respiration by plant and microbial biomass. The governing equation used to determine the partial pressure of a gas in a soil layer is the Van der Waals real gas equation (Equation 10.14):

$$PV = \frac{nRT}{V - nB} - \frac{A * n^2}{V^2} \quad (10.14)$$

where:

P = gas pressure in atmospheres

V = volume in the layer

R = gas constant

T = temperature in Kelvin

n = number of moles of the gas

A and B = constants for each gas.

Under some conditions, the simpler ideal gas Equation (10.15) can be used without loss of accuracy

$$PV = nRT \quad (10.15)$$

The atmospheric pressure in a layer is determined by summation of the partial pressures of each gaseous component. The pressure throughout the soil column is equalised to be at atmospheric pressure by transferring the necessary amounts of gas (in moles) between layers, starting from the deepest layer and working towards the surface.

10.8.2 Gas diffusion

If the amount of gas transfer by the atmospheric pressure equalisation process is small, gas diffusion across the soil layers is also simulated. This diffusion process follows Jury *et al.* (1991), as given in Equation (10.16):

$$\text{Gas Flux} = \frac{\text{Tut_Const} * \text{Diff_Rate} * \text{Gas_Con_Diff}}{\text{Distance}} \quad (10.16)$$

where:

Gas Flux = amount of gas in moles per second transferred between two adjacent layers

Tut_Const = soil tortuosity constant taken as (air volume)^{1.5}

Diff_Rate = Binary gaseous diffusion rate

Gas_Con_Diff = difference in gas concentration between the two layers

Distance = average distance between the two layers.

10.9 CaNS-Eff execution

10.9.1 *Modus operandi*

The operation of CaNS-Eff is as follows:

All state variables are known for the current time step $T(\text{cur})$. The changes in these state variables are calculated due to the various processes simulated for the next time step $T + dt$ (nxt). If the time iteration is considered to be successful, as discussed below, the next state (nxt) becomes the current state (cur) and time is incremented by dt . For a time step to be valid there are two criteria that must be met:

1. Mass of C and N over the time increment dt must be conserved
2. The rate of change in critical pools must be lower than a specified value.

The basis of this rate-checker is that the rate of change in a pool, for the current dt , is checked against a maximum allowable change. This value is specified as a percentage of the maximum amount that has been in the pool, i.e. the maximum allowable change is 1.5 times the highest amount the pool has previously had in it.

For example:

If a pool had a maximum amount of 20, and the maximum allowable percentage change was set at 10%, then $20 \cdot 0.1 \cdot 1.5 = 3$ units is the maximum allowable change. The rate-checker is applied over a number of user-specified critical pools.

If the current rate of change is higher than that allowed, dt is dropped back and the simulation repeated until the rate of change is less than the maximum allowable rates or minimum dt . On start-up, minimum dt is used, as the maximum allowable change in the critical pools is initialised as zero.

Rate-checkers also check for negatives in all pools. A long time step with a high rate of extraction can cause the pool size to drop below zero. By reducing the time step, with the same rate of extraction over a shorter time period, the negative is avoided. This process tends to be the dominant control on the size of dt .

10.9.2 Order of execution in CaNS-Eff

The soil hydrology model is run first and an output file produced with time stamps, soil water tension and the fluxes between computational node points. Inter-layer processes are simulated starting with transport of materials between layers including particulate DFE components and the dissolved components in the mesopore water. The dissolved fraction moved is considered to be instantaneously mixed. Once inter-layer solute movement is complete, inter-layer diffusion occurs in both the micropore and mesopore domains.

The intra-layer processes, such as diffusion between micropore and mesopore, are simulated and adsorption kinetics using the non-equilibrium adsorption curves for the micropore and mesopore domains are determined.

Competition for the substrates ammonium, nitrate and oxygen between plant and microbial biomass competitors is solved so that the resource allocation is known. Microbial dynamics are simulated as discussed in Section 10.4, followed by the plant growth and uptake processes.

The calculated changes of state variables are applied, and the rate of change of critical pools and conservation of mass is checked to determine if the predicted next state is a valid solution.

The soil gas model is applied over the soil profile, once a successful solution is found, and the model is ready for the next time step.

10.1 Technical specifications

CaNS-Eff is written in GCC(2.95-2.96)C++ language within a LINUX (Redhat Linux 6.2) environment running on a P2 MMX 330 MHz PC. The CaNS-Eff model is built from approximately 70 files that contain in total 25,000 lines of code.

The graphical user interface is provided through Xforms (0.88). This interface has two screens, the main graphical interface (Figure 10.3), which reports on six variables down the entire profile. A second output screen (Figure 10.4) shows for one selected layer the change in the six variables with time.

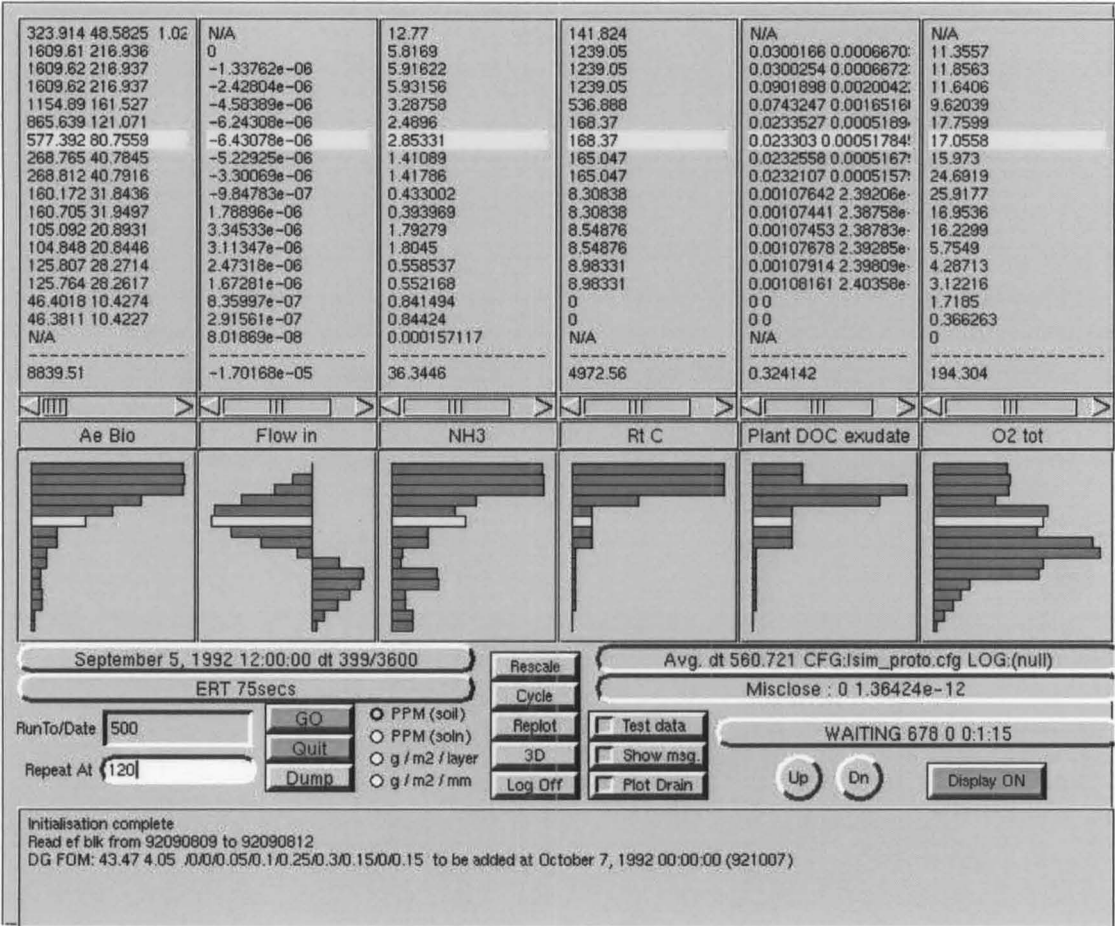


Figure 10.3 Main graphical interface for the CaNS-Eff model, showing the six selected variables down the entire profile.

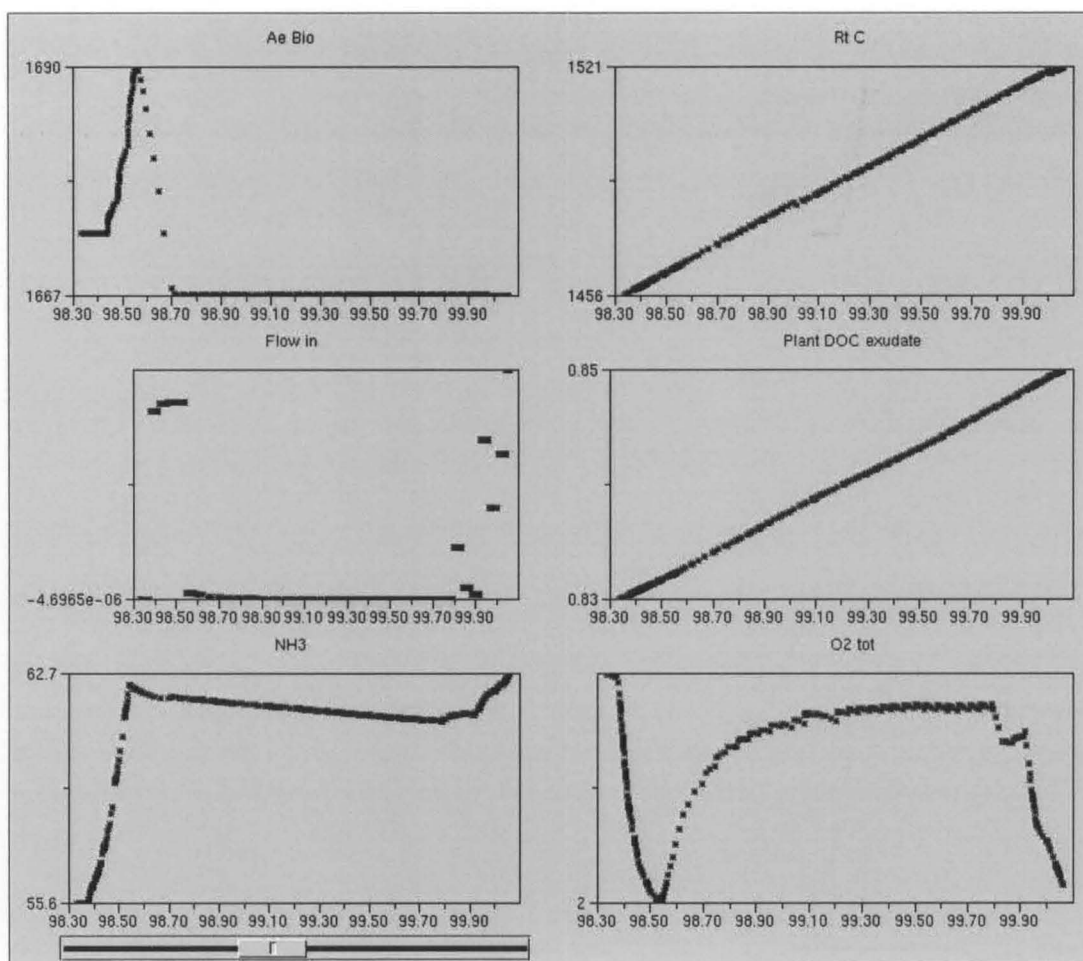


Figure 10.4 Secondary graphical interface for CaNS-Eff model, showing the six selected variables for one layer with time.

In the current version of CaNS-Eff there are 167 variables which can be displayed on the interface. Any number of these variables may be logged to output files for subsequent analysis. The units for the C and N variables can be g g^{-1} soil, g g^{-1} water, g layer^{-1} or g mm^{-1} .

10.11 References

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Chapter Eleven

Parameterisation of the CaNS-Eff model to describe the fate of DFE applied onto the land

The objective of this Chapter is to:

Explain the derivation of the parameter set chosen to use in CaNS-Eff to simulate the fate of C and N from DFE applied onto the conventionally drained DFE-irrigated lysimeters

11.1 Introduction

This Chapter discusses the selection of parameters to use with CaNS-Eff to simulate the fate of C and N from DFE irrigated onto conventionally drained lysimeters (0-treatment) from September 1992 to March 1996.

11.2 Basic availability structure

The microbial availability of C in a pool is described by the availability structure. Presently, the availability structure has nine availability bins, each with a decay constant as given in Table 11.1.

Table 11.1 **Availability bins to describe the microbial availability.**

Bin number	Bin label	Decay constant (day ⁻¹)	Half-life (days or years)
0	Glucose	8.6E4	8.1E-6 days
1	Labile cell material	0.1	7 days
2	Hemi-cellulose	0.075	9 days
3	Cellulose	0.05	14 days
4	Lignin	0.008	87 days
5	Microbial cell wall material	0.004	173 days
6	Waxes and fatty acids	0.0006	2.4 years
7	Phenols	0.0002	6.3 years
8	Stabilised organic matter	1.0E-6	760 years

11.3 Decay constants for availability bins

Two types of data have been used to select the decay constants for each of the availability bins as given in Table 11.1. The first source of data is from laboratory studies, where substrate has been added to the soil and the decomposition rate of the added substrate determined from CO₂ evolution. Estimates of the decomposition rate made in this manner must be corrected for microbial biomass production and recycling of added substrate by using Equation (11.1) (Paul and van Veen, 1979).

$$\text{Actual decomposition} = \text{CO}_2 \text{ produced} \times \left(\frac{1 + \text{eff}}{1 - \text{eff}} \right) \quad (11.1)$$

where:

eff = efficiency of the use of C for biosynthesis, as a percentage of total C uptake

CO₂ produced = CO₂ evolved during decomposition of the substrate.

Non-cell metabolite production is ignored in this analysis. The period over which CO₂ evolution was measured in the laboratory experiment is reported here so that an assessment can be made of the opportunity for recycling of the original substrate.

The second source of information is from modelling studies, where decay rates have been assigned to materials similar to those used in the availability bins. Such data must be used with some caution, however, as there is a risk that different interpretations and implementation methods can require parameters to be fitted that reflect the method implemented as opposed to the actual bio-availability of the material.

11.3.1 Bin 0: Glucose

The decay constant has been set at 1 s^{-1} (86400 day^{-1}) to reflect that glucose is immediately available for microbial consumption.

11.3.2 Bin 1: Labile cell material

Table 11.2 Experimental data for the decay of labile cell material.

Name of material	Original data source (if different from reported source)	Length of expt. (days)	Reported by	Decay constant (day^{-1})	Efficiency (%)
Amino acids	Verma <i>et al.</i> (1975)	7	Paul and van Veen, (1979)	0.2-0.5	20
Plant solubles	Simonart and Mayaudon (1958)	10	Paul and van Veen, (1979)	0.09	20
Acetate	Sørensen and Paul (1971)	5	Paul and van Veen, (1979)	0.14	60
	Sørensen and Paul (1971)	5	Paul and van Veen, (1979)	0.06	20
Fungal cytoplasm	Hurst and Wagner (1969)	10	Paul and van Veen, (1979)	0.17	60
Cell proteins	Verma <i>et al.</i> (1975)	7	Paul and van Veen (1979)	0.13	20
Cytoplasm – rapid fraction (50% of C)	_____	N/A	Juma and McGill (1986)	0.27	N/A
Cell wall – rapid fraction (40% of C)	_____	N/A	Juma and McGill (1986)	0.12	N/A

Table 11.3 Decay constants used in previous model studies to describe first-order decomposition of labile cell material.

Name of pool	Model	Decay constant (day ⁻¹)	Source
Soluble slurry fraction	AMINO	0.082	Berghuijs van Dijk <i>et al.</i> (1985)
Metabolic added organic matter (AOM ₂)	DAISY	0.07	Hansen <i>et al.</i> (1991)
Soluble	Unnamed	0.20	Paul and van Veen (1979)
Metabolite	TRAMIN	1.0	Juma and Paul (1981)
Well decomposable	Unnamed	0.8	van Veen <i>et al.</i> (1985)

The decay constants used in previous modelling studies for labile material covered a wide range from 0.07 to 1.0 day⁻¹, while the experimental data had a narrower range of 0.06 to 0.5 day⁻¹. With most of the experimental data being in the range of 0.06 to 0.17 day⁻¹, the decay constant for the labile cell material was set at 0.10 day⁻¹.

11.3.3 Bin 2: Hemi-cellulose

Table 11.4 Experimental data for the decay of hemi-cellulose.

Name of material	Original data source (if different from reported source)	Length of expt. (days)	Reported by	Decay constant (day ⁻¹)	Efficiency (%)
Hemi-cellulose	Simonart and Mayaudon (1958)	10	Paul and van Veen (1979)	0.11	20
Hemi-cellulose	Cheshire <i>et al.</i> (1974)	10	Paul and van Veen (1979)	0.04	20
Hemi-cellulose	Cheshire <i>et al.</i> (1974)	10	Paul and van Veen (1979)	0.11	60
Hemi-cellulose	Minderman (1968)	365	Paul and van Veen (1979)	0.006	20
Hemi-cellulose	_____	N/A	Killham (1994)	0.07	N/A

Table 11.5 Decay constants used in previous model studies to describe first-order decomposition of hemi-cellulose.

Name of pool	Model	Decay constant (day ⁻¹)	Source
Hemi-cellulose	PAPRAN	0.05	Seligman and van Keulen (1981)
Hemi-cellulose	Unnamed	0.08	Paul and van Veen (1979)
Slowly decomposable C	TRAMIN	0.10	Juma and Paul (1981)

There was very good agreement between the experimentally derived decay constants and the model parameters for hemi-cellulose. The decay constant of 0.075 day⁻¹ used in CaNS-Eff was based on the average of all the data, ignoring the one very low value.

11.3.4 Bin 3: Cellulose

Table 11.6 Experimental data for the decay of cellulose.

Name of material	Original data source (if different from reported source)	Length of expt. (days)	Reported by	Decay constant (day ⁻¹)	Efficiency (%)
Cellulose	Simonart and Mayaudon (1958)	10	Paul and van Veen (1979)	0.03	20
Cellulose	Simonart and Mayaudon (1958)	10	Paul and van Veen (1979)	0.08	80
Cellulose	Minderman (1968)	365	Paul and van Veen (1979)	0.004	20

Table 11.7 Decay constants used in previous model studies to describe first-order decomposition of cellulose.

Name of pool	Model	Decay constant (day ⁻¹)	Source
Cellulose	PAPRAN	0.05	Seligman and van Keulen (1981)
Fast cycling plant residue	DAISY	0.05	Hansen <i>et al.</i> (1991)
Fast cycling root residue	DAISY	0.07	Wu and McGechan (1998)
Roots decomposable	Unnamed	0.02	Paul and van Veen (1979)

As with hemi-cellulose, the experimental and the model data for the decay constants of cellulose were in good agreement. Hence the average value of 0.05 day⁻¹, ignoring the one very low value, was used as the decay constant for cellulose.

11.3.5 Bin 4: Lignin

Table 11.8 Experimental data for the decay of lignin.

Name of material	Original data source (if different from reported source)	Length of expt. (days)	Reported by	Decay constant (day ⁻¹)	Efficiency (%)
Lignin	Minderman, (1968)	365	Paul and van Veen (1979)	0.002	20
Lignin	_____	N/A	Killham (1994)	0.002	N/A

Table 11.9 Decay constants used in previous model studies to describe first-order decomposition of lignin.

Name of pool	Model	Decay constant (day ⁻¹)	Source
Lignified residues	Unnamed	0.009	van Veen and Paul (1981)
Lignin	PAPRAN	0.0095	Seligman and van Keulen (1981)
Lignin	Unnamed	0.01	Paul and van Veen (1979)

The value of 0.008 day⁻¹ was used for the decay constant of lignin. This value was based on the average (0.0095 day⁻¹) of the three close rates used in previous model studies, with a slight reduction to account for the two experimental values of 0.002 day⁻¹.

11.3.6 Bin 5: Microbial cell wall material

Table 11.10 Experimental data for the decay of microbial cell material.

Name of material	Original data source (if different from reported source)	Length of expt. (days)	Reported by	Decay constant (day ⁻¹)	Efficiency (%)
Fungal cell wall	Hurst and Wagner (1969)	10	Paul and van Veen (1979)	0.03	20
Fungal cell wall	Hurst and Wagner (1969)	10	Paul and van Veen (1979)	0.07	60
<i>A. Niger</i> cell wall	Hurst and Wagner (1969)	10	Paul and van Veen (1979)	0.09	20
Cell wall - slow fraction mixed (60% of C)	Nelson <i>et al.</i> (1979)	N/A	Juma and Paul (1981)	0.004	N/A
Cytoplasm-slow fraction mixed (40% of C)	Nelson <i>et al.</i> (1979)	N/A	Juma and Paul (1981)	0.005	N/A

Table 11.11 Decay constants used in previous model studies to describe first-order decomposition of pools similar to microbial cell material.

Name of pool	Model	Decay constant (day ⁻¹)	Source
Active fraction	TRAMIN	0.004	Juma and Paul (1981)
Microbial products	Unnamed	0.04	Paul and van Veen (1979)
Recalcitrant microbial metabolites	Unnamed	0.3	van Veen <i>et al.</i> (1985)

There was an extremely high range in the decay constants of microbial cell material used in previous modelling studies (0.3 to 0.004 day⁻¹) as well as in the experimental data (0.03 to 0.005 day⁻¹). The value

chosen (0.004 day^{-1}) was based on the work by Juma and Paul (1981), in which this experimentally derived value was used successfully in a model study.

11.3.7 Bin 6: Waxes and fatty acids

Table 11.12 Experimental data for the decay of waxes and fatty acids.

Name of material	Original data source (if different from reported source)	Length of expt. (days)	Reported by	Decay constant (day^{-1})	Efficiency (%)
Waxes	Minderman (1968)	365	Paul and van Veen (1979)	$8.0\text{E-}4$	20

Table 11.13 Decay constants used in previous model studies to describe first-order decomposition of pools similar to waxes and fatty acids.

Name of pool	Model	Decay constant (day^{-1})	Source
Resistant residues	Rothamsted	$8.2\text{E-}4$	Jenkinson and Rayner (1977)
Stabilised organic matter	TRAMIN	$6.0\text{E-}4$	Juma and Paul (1981)

There was good agreement between all data for the decay constants for waxes and fatty acids. The value of $6.0\text{E-}4 \text{ day}^{-1}$ from Juma and Paul (1981) was chosen for reasons of consistency with the parameterisation of Bin 5.

11.3.8 Bin 7: Phenols

Table 11.14 Experimental data for the decay of phenols.

Name of material	Original data source (if different from reported source)	Length of expt. (days)	Reported by	Decay constant (day^{-1})	Efficiency (%)
Phenols	Minderman (1968)	365	Paul and van Veen (1979)	$3.0\text{E-}4$	20

Table 11.15 Decay constants used in previous model studies to describe first-order decomposition of pools similar to phenols.

Name of pool	Model	Decay constant (day^{-1})	Source
Resistant compounds (SOMZ)	DAISY	$1.4\text{E-}4$	Hansen <i>et al.</i> (1991)
Active protected SOM	Unnamed	$9.5\text{E-}5$	van Veen and Paul (1981)
Active	CENTURY	$4.6\text{E-}4$	Parton <i>et al.</i> (1987)

The decay constant for phenols was set at $2.0\text{E-}4 \text{ day}^{-1}$ based on the average of all data.

11.3.9 Bin 8: Stabilised organic matter

Ignoring the single high value, the decay constant for stabilised organic matter was set at 1.0E-6 day⁻¹ based on the other four rate constants used in previous modelling studies, as reported in Table 11.16.

Table 11.16 Decay constants used in previous model studies to describe first-order decomposition of pools similar to stabilised organic matter.

Name of pool	Model	Decay constant (day ⁻¹)	Source
Chemically stabilised (SOM ₁)	DAISY	2.7E-6	Wu and McGechan (1998)
Passive	CENTURY	2.2E-6	Parton <i>et al.</i> (1987)
Old organic matter	TRAMIN	3.0E-6	Juma and Paul (1981)
Stable organic matter	PAPRAN	8.3E-5	Seligman and van Keulen (1981)
Old organic matter	Unnamed	9.2E-7	van Veen and Paul (1981)

11.4 Percentage of C in each of the availability bins

There are thirteen organic matter pools represented in CaNS-Eff. Of these, eight are microbial substrates requiring an availability structure. The decay constants for each of the availability bins, representing a carbon compound, has been determined in Section 11.3 (Table 11.1). The percentage of the total carbon in each bin was determined by reviewing relevant laboratory and modelling studies described below. As the decay constants reported in the literature studies were not generally the same as the constants used in the availability bins in CaNS-Eff, some translation was required to enable estimates of the percentage of organic matter in various bins to be made from this data.

11.4.1 Native soil organic matter

The *native soil organic matter* pool is part of the POM class. Relevant literature values to describe this material are given in Table 11.17.

Table 11.17 Summary of reported data on the C percentages in materials or pools similar to *native soil organic matter*.

Study or model data	Reference
<u>Soil organic matter</u> 50% aromatic C 15% carbohydrate C 15% fatty acids 20% associated with N	Killham (1994)
<u>Soil organic matter</u> 60% carbohydrates i.e. 20-50% cellulose 10-30% hemi-cellulose 1-5% sugars and starches 1-15% water soluble and crude protein 10-30% lignins 1-8% fats, waxes, tannins	Waksman (1948)
<u>Soil organic matter</u> 10-20% carbohydrates 20% amino acids/proteins 50% complexed aromatic phenolic and carboxylic acids 10-20% long chain fatty acids, cell wall components	Paul and van Veen (1979)
<u>DAISY</u> 80% SOM ₁ , slow pool of native soil organic matter, $k = 2.7\text{E-}6 \text{ day}^{-1}$ 19.4% SOM ₂ , faster pool of native soil organic matter, $k = 1.4\text{E-}4 \text{ day}^{-1}$	Hansen <i>et al.</i> (1991)
70% SOM ₁ 30% SOM ₂	Svendsen <i>et al.</i> (1995)
<u>TRAMIN</u> 5% active fraction $k = 3.7\text{E-}3 \text{ day}^{-1}$ 40% stabilised $k = 6.0\text{E-}4 \text{ day}^{-1}$ 55% old $k = 3.0\text{E-}6 \text{ day}^{-1}$	Juma and Paul (1981)

This information on carbon fractionation for various published decay constants and for different compounds in soil organic matter has been used to estimate the percentages of carbon in each of the availability bins used in the *native soil organic matter* pool (Table 11.18).

Table 11.18 Carbon percentages in various availability bins for *native soil organic matter*.

Bin number	Bin label	% C in bin	Decay constant (day ⁻¹)
4	Lignin	15	0.008
5	Microbial cell wall material	15	0.004
6	Waxes and fatty acids	15	0.0006
7	Phenols	20	0.0002
8	Stabilised organic matter	35	1.0E-6

11.4.2 Particulate DFE fraction

The particulate fraction of the DFE belongs to the POM class. Relevant studies on the carbon percentages in various fractions for materials similar to the particulate fraction of DFE are summarised in Table 11.19.

Table 11.19 Summary of reported data on the C percentages in materials or pools similar to *particulate DFE fraction*.

Study or model data	Reference
<u>Van Soest fibre analysis on faeces samples</u>	
20% lignin	Analysis of 29 dairy cow faeces sampled throughout milking season in the Waikato (Barkle, unpublished data)
42% hemi-cellulose	
38% cellulose	
<u>Incubation studies</u>	
30% of C as CO ₂ from DFE in first 50 days $k = 0.0105\text{E-}3 \text{ day}^{-1}$ with 20% efficiency 70% stabilised	Barkle <i>et al.</i> (2001)
35% of C as CO ₂ from DFE in first 180 days $k = 2.3\text{E-}3 \text{ day}^{-1}$	Stenger <i>et al.</i> (2001)
Feedlot waste	Reddy <i>et al.</i> (1980)
24% of C $k = 3.0\text{E-}2 \text{ day}^{-1}$	
9% of C $k = 9.8\text{E-}3 \text{ day}^{-1}$	
67% of C $k = 3.6\text{E-}3 \text{ day}^{-1}$	
<u>AMINO</u>	
Cattle slurry (non dissolved fractions only)	Berghuijs van Dijk <i>et al.</i> (1985)
76% partly dissolved fresh $k = 2.7\text{E-}3 \text{ day}^{-1}$	
23% slowly decomposing $k = 3.3\text{E-}4 \text{ day}^{-1}$	
<u>DAISY</u>	
Farmyard manure	Jensen <i>et al.</i> (1997)
18% $k = 5.0\text{E-}2 \text{ day}^{-1}$	
72% $k = 5.0\text{E-}3 \text{ day}^{-1}$	
10% $k = 1.4\text{E-}4 \text{ day}^{-1}$	
<u>SOILN</u>	
Animal faeces	Wu and McGechan (1998)
100% $k = 3.5\text{E-}2 \text{ day}$	

The percentages of carbon in each of the availability bins for the *particulate DFE fraction* are given in Table 11.20.

Table 11.20 Carbon percentages in various availability bins for *particulate DFE fraction*.

Bin number	Bin label	% C in bin	Decay constant (day ⁻¹)
3	Cellulose	5	0.05
4	Lignin	5	0.008
5	Microbial cell wall material	5	0.004
6	Waxes and fatty acids	10	0.0006
7	Phenols	25	0.0002
8	Stabilised organic matter	50	1.0E-6

11.4.3 Root exudates

Root exudates are the C rich components released into the soil by growing roots. Two studies that discuss its carbon composition are summarised in Table 11.21. *Root exudates* are part of the DOMhighCN class.

Table 11.21 Summary of reported data on the C percentages in *root exudates*.

Study or model data	Reference
<u>Root exudates</u>	
44% soluble C	Darrah (1997)
- monosaccharides	
- amino acids	
56% insoluble C	
- mucilages	
- dead root hairs	
- sloughed off cortical cells	
13% root cap material	
87% mucilage	
<u>Root exudates from barley</u>	
<i>Abee</i> variety	Xu and Juma (1995)
87% $k = 0.161 \text{ day}^{-1}$	
13% $k = 0.018 \text{ day}^{-1}$	
<i>Samson</i> variety	
74% $k = 0.154 \text{ day}^{-1}$	
26% $k = 0.023 \text{ day}^{-1}$	

Using the reported data on the type of carbon compounds present and the percentages of carbon for various published decay constants, the amounts in each of the availability bins used in CaNS-Eff for the *root exudates* pool are given in Table 11.22.

Table 11.22 Carbon percentages in various availability bins for *root exudates*.

Bin number	Bin label	% in bin	Decay constant (day ⁻¹)
1	Labile cell material	70	0.1
3	Cellulose	20	0.05
5	Microbial cell wall material	10	0.004

11.4.4 Dead microbial biomass

Dead microbial biomass is available for microbial consumption and is part of the FOM class. The degradation of this necromass is assumed to be extracellular and published data on the decomposition of this material are given in Table 11.23.

Table 11.23 Summary of reported data on the C percentages in *dead microbial biomass*.

Study or model data		Reference
<u>Soil incubation studies</u>		
Typic Cryoboralf, Canada and Ochreptic Hapludalf, France		Juma and McGill (1986)
70%	$k = 0.32 \text{ day}^{-1}$	
30%	$k = 6.6\text{E-}3 \text{ day}^{-1}$	
<u>Model study</u>		
60% well decomposable pool	$k = 0.80 \text{ day}^{-1}$	van Veen <i>et al.</i> (1985)
40% recalcitrant metabolites	$k = 0.30 \text{ day}^{-1}$	
<u>Model study</u>		
100% dead microbial biomass	$k = 0.04 \text{ day}^{-1}$	Paul and van Veen (1979)
<u>TRAMIN</u>		
50% metabolites	$k = 1.0 \text{ day}^{-1}$	Juma and Paul (1981)
50% active	$k = 3.7\text{E-}3 \text{ day}^{-1}$	
<u>Model study</u>		
100% max rate	$k = 1.2 \text{ day}^{-1}$	Darrah (1997)

The percentages of carbon in each of the availability bins for *dead microbial biomass* are given in Table 11.24.

Table 11.24 Carbon percentages in various availability bins for *dead microbial biomass*.

Bin number	Bin label	% C in bin	Decay constant (day ⁻¹)
0	Glucose	18	8.6E4
1	Labile cell material	40	0.1
5	Microbial cell wall material	42	0.004

11.4.5 Dissolved DFE OM high C:N

Dissolved organic compounds with a high C:N ratio in DFE are part of the *dissolved DFE OM high C:N* pool. Relevant studies on the composition of this pool are summarised in Table 11.25.

Table 11.25 Summary of reported data on the C percentages in materials or pools similar to *dissolved DFE OM high C:N*.

Study or model data	Reference
<u>Soil incubation study</u> DOC fraction from faeces and urine behaved like glucose.	Chapter 3 of this work.
<u>ANIMO</u> 100% soluble slurry	$k = 8.2\text{E-}2 \text{ day}^{-1}$ Berghuijs van Dijk <i>et al.</i> (1985)

Based on this information the availability structure implemented for *dissolved DFE high C:N* pool is given in Table 11.26.

Table 11.26 Carbon percentages in various availability bins for *dissolved DFE OM high C:N* and *dissolved DFE OM low C:N*.

Bin number	Bin label	% in bin	Decay constant (day ⁻¹)
0	Glucose	25	8.6E4
1	Labile cell material	50	0.1
2	Hemi-cellulose	25	0.075

11.4.6 *Dissolved DFE OM low C:N*

In studies involving dissolved fractions of organic materials the high and low C:N ratio materials are not considered separately but as one dissolved material. Until further data are available it has been assumed that the *dissolved DFE low OM C:N* pool has the same availability as that of the *dissolved DFE high OM C:N* pool, as given in Table 11.26.

11.4.7 *Dead foliage biomass*

Published data on the percentages of C in various C compounds or decay pools in dead foliage are summarised in Table 11.27. The *dead foliage biomass* pool is in the FOM class and is made up of cut foliage or foliage which has died due to extreme environmental conditions.

Table 11.27 **Summary of reported data on the C fractions in *dead foliage biomass*.**

Study or model data	Reference	
<u>Van Soest fibre analysis</u>		
White clover	Kumar K. (1998, pers. comm.)	
41% cellulose		
45% hemi-cellulose		
10% lignin		
4% phenols		
Ryegrass		
25% cellulose		
56% hemi-cellulose		
17% lignin		
2% phenols		
<u>Van Soest fibre analysis</u>		
	Henriksen and Breland (1999)	
White clover		
49.8% cellulose		
41.3% hemi-cellulose		
8.8% lignin		
Ryegrass		
54.5% cellulose		
42.9% hemi-cellulose		
2.6% lignin		
<u>Soil incubation studies</u>		
	Juma and McGill (1986)	
Ryegrass (England)		
70%		$k = 7.9\text{E-}3 \text{ day}^{-1}$
30%		$k = 2.3\text{E-}4 \text{ day}^{-1}$
Ryegrass (Nigeria)		
70%		$k = 2.6\text{E-}2 \text{ day}^{-1}$
30%		$k = 1.1\text{E-}3 \text{ day}^{-1}$
Medic (Australia)		
68%		$k = 6.2\text{E-}2 \text{ day}^{-1}$
32%		$k = 5.2\text{E-}4 \text{ day}^{-1}$
<u>Soil incubation study</u>		
	Breland (1994)	
White clover		
60%		$k = 0.129 \text{ day}^{-1}$
40%		$k = 3.4\text{E-}4 \text{ day}^{-1}$
<u>Soil incubation study</u>		
	Simonart and Mayaudon (1958)	
Ryegrass		
20%		$k = 0.06 \text{ day}^{-1}$
60%		$k = 0.23 \text{ day}^{-1}$

Based on information in Table 11.27, the percentages of carbon in the availability bins used to describe *dead foliage biomass* are given in Table 11.28.

Table 11.28 Carbon percentages in various availability bins for *dead foliage biomass*.

Bin number	Bin label	% C in bin	Decay constant (day ⁻¹)
2	Hemi-cellulose	40.0	0.075
3	Cellulose	20.0	0.05
4	Lignin	30.0	0.008
7	Phenols	10.0	0.0002

11.4.8 *Dead root biomass*

Information on the carbon components in *dead root biomass*, which belongs to the FOM class, is summarised in Table 11.29.

Table 11.29 Summary of reported data on the C percentages in *dead root biomass*.

Study or model data	Reference
<u>Van Soest fibre analysis</u>	Whitehead <i>et al.</i> (1979)
Ryegrass roots	
54% cell wall	
19% cellulose	
21% hemi-cellulose	
5% lignin	
1% soluble proteins	
Red clover roots	
63% cell wall	
31% cellulose	
14% hemi-cellulose	
14% lignin	
7% soluble proteins	
<u>Van Soest fibre analysis</u>	McGill <i>et al.</i> (1981)
Ryegrass roots	
25-30% hemi-cellulose	
25-30% cellulose	
15-20% lignin	
5-10% protein	
5-12% waxes	
<u>AMINO</u>	
Root material	$k = 6.0\text{E-}4 \text{ day}^{-1}$ Berghuijs van Dijk <i>et al.</i> (1985)
<u>DAISY</u>	
40%	$k = 7.0\text{E-}3 \text{ day}^{-1}$ Svendsen <i>et al.</i> (1995)
60%	$k = 7.0\text{E-}2 \text{ day}^{-1}$

Based on information in Table 11.29 the percentages of carbon in each of the availability bins for *dead root biomass* are given in Table 11.30.

Table 11.30 Carbon percentages in various availability bins for *dead root biomass*.

Bin number	Bin label	% C in bin	Decay constant (day ⁻¹)
1	Labile cell material	2	0.1
2	Hemi-cellulose	20	0.075
3	Cellulose	20	0.05
4	Lignin	4	0.008
5	Microbial cell wall material	54	0.004

11.5 Basic soil and microbial distribution data

The model is divided into 16 soil layers based on soil physical, chemical and biological data collected during lysimeter construction. Data by soil horizon on soil bulk densities, biomass concentrations, NH₄, NO₃, Total N and Total C concentrations are shown in Table 11.31.

Table 11.31 Soil chemistry and initial microbiological data for model.

Horizon number	Horizon name	Horizon depth (mm)	Bulk density (kg m ⁻³)	Total N (%)	Total C (%)	Biomass (g m ⁻³)	NH ₄ -N (g m ⁻³)	NO ₃ -N (g m ⁻³)
1	Apg	0-50	1063	0.44	5.50	1666	2.23	7.30
2	Ap1	50-100	1209	0.30	3.90	1200	0.83	4.87
3	Ap2	100-150	1209	0.21	2.40	900	0.97	3.90
4	Ap3	150-200	1209	0.19	2.40	600	2.00	5.10
5	Bgc	200-300	1233	0.13	1.32	282	1.13	5.33
6	Br1U	300-400	1138	0.06	0.55	173	0.27	1.33
7	Br1L	400-500	1106	0.04	0.33	113	1.77	2.47
8	Br2U	500-600	1053	0.03	0.22	137	0.43	1.33
9	Br2L	600-700	1108	0.01	0.16	51	0.80	0.70

11.6 Split between micropore and mesopore domains

Following the approach of RZWQM, (USDA-ARS, 1992) a tension of -200 kPa is used to differentiate between the micropore and mesopore domains. This tension equates to an idealised cylindrical pore diameter of 1.5 µm.

The mesopore volume is the total porosity minus the volumetric soil water content at the -200 kPa tension. The micropore volume is the volumetric water content at -200 kPa. The volumetric water content that this tension equates to was based on measured moisture release data obtained from undisturbed cores taken during the lysimeter collection. As the volumetric moisture contents were measured over a range from -0.4 to -1500 kPa but not at -200 kPa, the values at this tension were determined from a retentivity function

(Hutson and Cass, 1987) used to fit the water retention curve. The volumetric water contents in the micropore and mesopore domains per layer are given in Table 11.32.

Table 11.32 Split between micropore and mesopore domains. Volumetric water content at -200 kPa used to separate the domains.

Horizon name	Micropore water (%)	Total porosity (%)	Mesopore water (%)	Mobile water as % of total water	Immobile water as % of total water
Apg	32	57	25	57	44
Ap1	32	53	22	59	41
Bgc	30	55	25	55	45
Br1U	33	57	24	58	42
Br1L	39	59	20	66	34
Br2U	35	59	24	59	41
Br2L	33	57	25	57	43

11.7 Soil microbial biomass parameters

11.7.1 Fungi:bacteria ratio

The microbial biomass in CaNS-Eff is divided into three different functional microbial populations: heterotrophs, denitrifiers and nitrifiers. Both fungi and aerobic bacteria are considered to be heterotrophic biomass. However, as some of the characteristics of fungi and bacteria are different the distribution with depth of each of the species needs to be estimated from literature. Data on microbial biomass distribution and C:N ratios is summarised from a review by Degens (1998).

While some data exists for the fungi:bacteria ratio in the topsoil of pastoral soils, less data is available with depth. The best estimates are those obtained using microscope techniques to determine the volume of different groups. In New Zealand the fungi:bacteria ratio can vary between 0.92 to 1.74:1, averaging 1.33:1 in the top 10 cm (West and Slade, 1987). This value is in agreement with ratios of between 1.1 and 1.5 for other grasslands of the world. There is little reliable information on the distribution of this ratio with depth for pasture soils. It is generally reported that most fungi live in the topsoil and that the proportion of fungal biomass decreases sharply with depth (Madsen, 1995; Madsen and Ghiorse, 1993). Federle *et al.* (1990) showed that the proportion of bacteria increased two-fold relative to fungi between 0.5 and 1.7 m below the soil surface. Based on best available information, the estimated distribution of fungal and bacterial biomass with depth is given in Table 11.33.

Table 11.33 Estimated distribution of fungal and bacterial biomass with horizon depth.

Horizon depth (mm)	Horizon name	Fungi %	Bacteria %
0-50	Apg	55.0	45.0
50-100	Ap1	50.0	50.0
100-200	Ap2 & 3	40.0	60.0
200-300	Bgc	22.5	77.5
300-500	Br1	12.5	87.5
500-700	Br2	2.5	97.5

11.7.2 Distribution of biomass pools and changes with depth

No information was available on the population sizes of the heterotrophs, denitrifiers and nitrifiers within the soil. The best estimates of the proportions of each of these biomass populations could only be obtained by calculation of the numbers in each group. Direct measurements of bacteria suggest that there can be 10^9 to 10^{10} bacteria g^{-1} soil. Based on denitrification enzyme activities in Waikato soils (Bailey, 1997) it is expected there is an average of $5.9\text{E}7$ cells g^{-1} denitrifiers in the soil with a range between $9.0\text{E}5$ and $1.17\text{E}8$ cells g^{-1} soil. This represents approximately 6% of the bacteria present.

Based on potential nitrification rates in pasture soils throughout the Waikato, the nitrifier population is between $5.0\text{E}5$ cells g^{-1} to $14.7\text{E}6$ cells g^{-1} , averaging at $7.6\text{E}6$ cells g^{-1} or approximately 1.5% of the population.

The aerobic bacteria usually account for 85-95% of the bacterial biomass in moist, well-aerated soils (Hattori, 1973). Based on this information the estimated distribution of bacterial biomass is given in Table 11.34, with the mean value being used to initialise CaNS-Eff.

Table 11.34 **Estimated distribution of bacterial biomass.**

Bacterial biomass	Range of the total bacterial population (%)
Aerobes	85 to 95
Denitrifiers	0.1 to 11.7
Nitrifiers	0.1 to 1.5

11.7.3 C:N ratio for bacteria and fungi

Based on culture studies by Harris *et al.* (1997), Tate *et al.* (1988) and Jenkinson *et al.* (1976) the average C:N ratio of 14 different species of fungi and bacteria was found to be 9.8 for fungi (ranging from 5.9 to 14.2) and 4.3 for bacteria (ranging from 3.5 to 6.9).

11.7.4 Michaelis-Menten uptake kinetic parameters

For simulating the microbial uptake of various substrates, the enzyme kinetics implemented in CaNS-Eff requires the maximum uptake rate (V_{\max}) and the half rate constant (K_m), which is the concentration of substrate when the uptake rate is at half V_{\max} , to be specified.

For simulating the uptake of available C, McGill *et al.* (1981) used a V_{\max} of 8.6 day^{-1} for bacteria and 4.0 day^{-1} for fungi with K_m of 60 and 100 mg C l^{-1} , respectively. Coody *et al.* (1986), investigating the uptake of glucose by microorganisms, reported a V_{\max} of 2.8 day^{-1} with a K_m of 175 mg C l^{-1} . The values used in CaNS-Eff follow McGill *et al.* (1981) as they are presented in a form that can be split between the three microbial populations, but in consideration of Coody's results V_{\max} was reduced by 50%.

The ammonium uptake by microbial populations as described by McGill *et al.* (1981) has a V_{\max} of 0.01 day⁻¹ for bacteria and 0.005 day⁻¹ for fungi with K_m of 0.2 mg N l⁻¹ for both populations.

For nitrifiers, McGill *et al.* (1981) report a V_{\max} of 0.3 day⁻¹ with K_m of 1.1 mg N l⁻¹. In DAISY (Svendsen *et al.*, 1995), nitrification was simulated with a V_{\max} of 5.0E-3 day⁻¹ and a K_m of 5 mg N l⁻¹. Smith (1982) measured a V_{\max} of 1.92 day⁻¹ with a K_m of 2.9 mg N l⁻¹ for *Nitrosomonas* spp. The upper value for nitrification rate with a V_{\max} of 1.92 day⁻¹ as reported by Smith (1982) was used in CaNS-Eff.

Based on measurements of potential denitrification on the actual lysimeter soils, and estimating that the denitrifier population represents 6% of the bacterial population, the measured V_{\max} for nitrate uptake was 2.0 g N g biomass-C⁻¹ day⁻¹. McGill *et al.* (1981) used a V_{\max} of 0.1 g N g biomass-C⁻¹ day⁻¹ with a K_m of 170 mg N l⁻¹ for simulating nitrate uptake by denitrifiers. Ranges for V_{\max} reported by Wu and McGechan (1998) are between 0.027 to 0.2 g N g biomass-C⁻¹ day⁻¹ with a K_m of 5 mg N l⁻¹. The values used in CaNS-Eff for nitrate uptake by denitrifiers are 0.1 g N g biomass-C⁻¹ day⁻¹ for the V_{\max} with a K_m of 5 mg N l⁻¹.

11.7.5 Respiration rates

There are two respiration rates specified for each of the biomass populations: the dormant C requirement and the respiration rate during active growth phase. Anderson and Domsch (1985a) measured the maintenance C requirements for dormant microbial biomass in two agricultural soils to be 1.7E-4 and 3.4E-4 mg glucose-C mg biomass-C⁻¹ hr⁻¹ at 28°C. These values were two to three orders less than that for pure cultures or metabolically active populations measured under *in situ* conditions. Smith and Paul (1990) reported similar maintenance values ranging from 1.0 to 1.9 E-4 hr⁻¹, again two to three times lower than those for active organisms. McGill *et al.* (1981) who reviewed four *in situ* studies on the maintenance rate for soil organisms used a value of 1.25E-4 hr⁻¹ for their maintenance rate in the PHOENIX model. The maintenance requirement for aerobes and denitrifiers used in CaNS-Eff is 1.8E-4 hr⁻¹ substrate-C biomass-C hr⁻¹.

Smith (1982) reported that the N used by nitrifiers for maintenance requirements, is an order of magnitude higher than that for the total soil microbial biomass. The value of 1.8E-3 mg substrate-C mg biomass-C hr⁻¹ was used in CaNS-Eff for the maintenance requirement for nitrifiers.

The growth respiration rate, which is defined as the respiration rate for an active population, was reported to be 3.0E-4 hr⁻¹ by Smith and Paul (1990). Anderson and Domsch (1985b) reported the growth respiration rate to be 1.2E-2 hr⁻¹. Darrah (1997) based on *in situ* measurements of two agricultural soils used a value of 1.65E-2 hr⁻¹ in his modelling work. McGill *et al.* (1981), after reviewing 13 field measurements of the net microbial growth rate in soil, used a value of 1.6E-2 hr⁻¹. Given the rather large variation in the reported values for this parameter, a mid range value of 3.6E-3 mg substrate-C mg biomass-C hr⁻¹ was used in CaNS-Eff. As no data were available on the growth rate to use for nitrifiers, a similar relativity between maintenance and growth rate as used for the aerobes and denitrifiers was used for the nitrifiers.

11.7.6 Soil temperature effects on microbial dynamics

There are numerous references available for the effect of temperature on microbial dynamics; two examples are given in Figure 11.1. One is from McGill *et al.* (1981), assuming that equal numbers of bacteria and fungi exist in the top 20 cm and the other is from Hutson and Wagenet (1992) for a moderate climate, normalised for the same format as that used by McGill *et al.* (1981). The moderate climate temperate response as described by Hutson and Wagenet (1992) was used in the CaNS-Eff model.

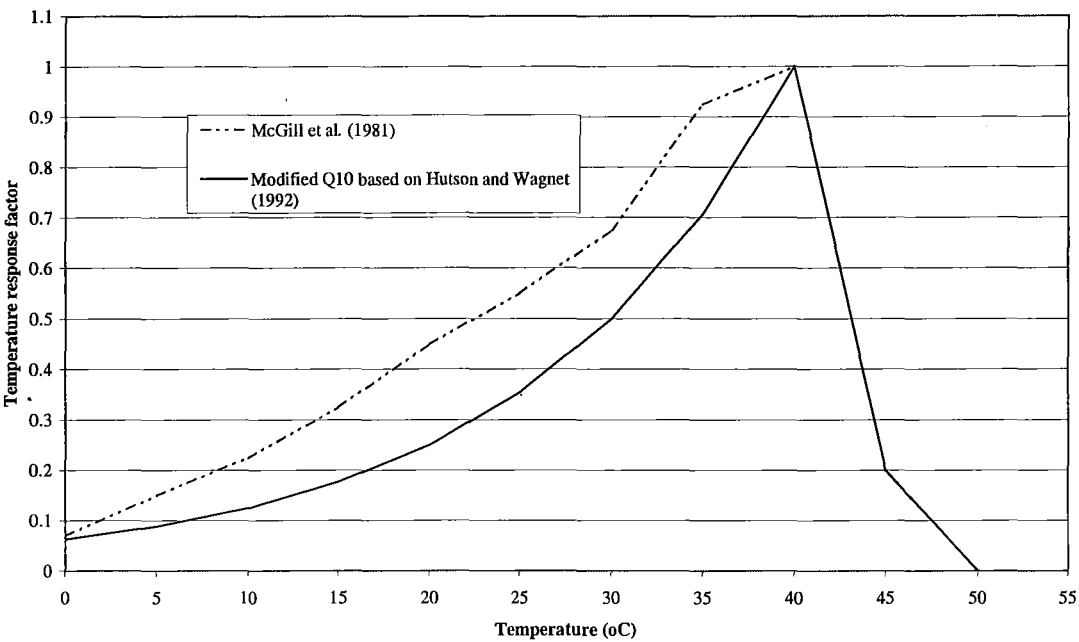


Figure 11.1 Soil temperature effect on microbial dynamics, after McGill *et al.* (1981) and Hutson and Wagenet (1992).

11.7.7 C:N ratio effects on microbial dynamics

There are two C:N ratio effects on microbial dynamics, one for C and the other for inorganic N uptake. The relationships used for CaNS-Eff are based on McGill *et al.* (1981) but modified for the optimum C:N ratio for microbial biomass, as given in Figure 11.2.

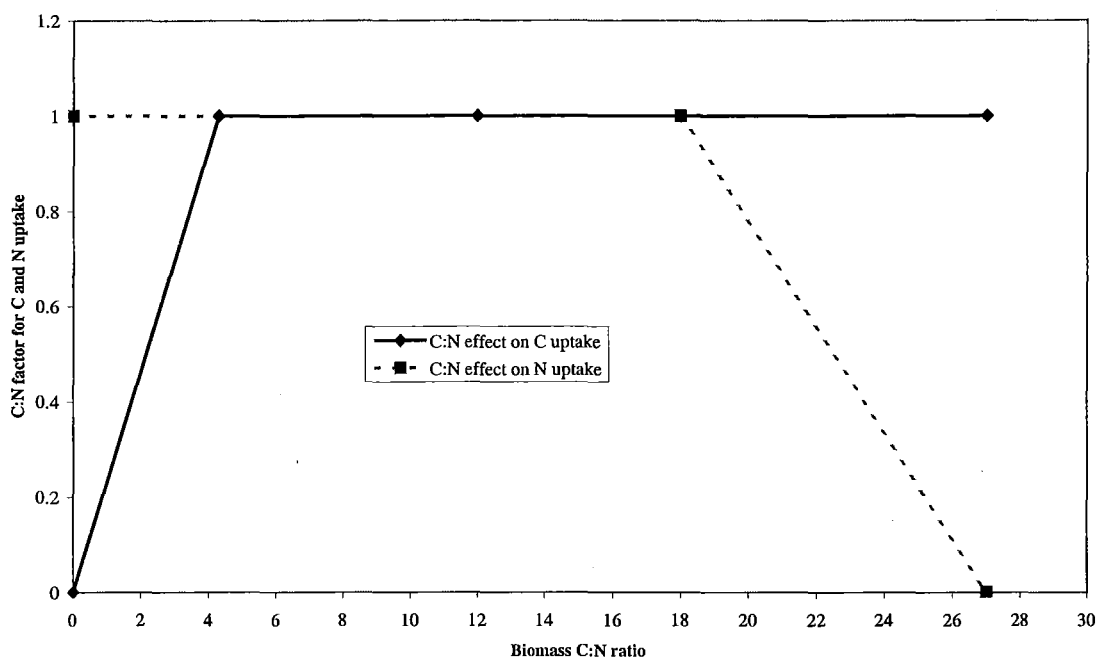


Figure 11.2 C:N effects on microbial dynamics for C and N uptake (McGill *et al.* 1981).

11.7.8 Microbial biomass growth and death parameters

Based on laboratory data (Chapter 3), the time that excess C must be available to induce microbial biomass growth was set at 2 hours.

The amount of the organic N incorporated into the microbial biomass is dependent on the C:N ratio of the biomass. If the biomass is N rich, indicated by the C:N ratio being 1 unit or more below the optimum, then 10% of the organic N associated with the C respiration is incorporated into the biomass. If the biomass is N poor, indicated by a C:N ratio being one unit or more above the optimum, then 90% of the organic N will be incorporated. CaNS-Eff interpolates between these values when the C:N ratio is within 1 unit of the optimum. The remaining N, which is not incorporated into microbial biomass is mineralised as soil NH_4 .

When microbial respiration is limited by an oxygen shortfall, the amount of biomass to kill off is five times the respiration shortfall.

11.7.9 Conversion terms

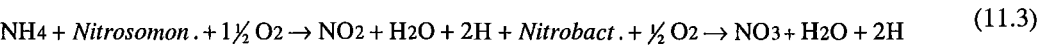
CaNS-Eff converts the NH_4 required by the nitrifiers to an equivalent C demand to allow the same computational methods for microbial growth and respiration to be used by all microbial populations. The conversion is based on the energy yield from a mole of glucose being 280 kcal (Killham, 1994), and for one mole of NH_4 the energy yield to the nitrifiers (*Nitrosomonas* and *Nitrobacter*) is 83 kcal. Hence, one mole of glucose is equivalent on an energy basis to 3.37 moles of NH_4 . Correcting for atomic mass on the basis of N being 77% of the 18 g mole^{-1} in NH_4 and C being 34% of the 212 g mole^{-1} in the glucose, results in 1 g of C being equivalent to 0.654 g of N as NH_4 .

The nitrate used by the denitrifiers under anaerobic conditions is also compared to an equivalent C mass oxidised under aerobic conditions. Firestone (1982) reports that 1.6 adenosine triphosphate (ATP) molecules are generated for every two electrons used during NO₃ reduction to N₂, compared to three ATP per two electrons from O₂ reduction. This makes aerobic oxidation 1.9 times more efficient than NO₃ reduction. The stoichiometry of nitrate reduction, as given in Equation (11.2), requires two moles of N for every three moles of C oxidised.



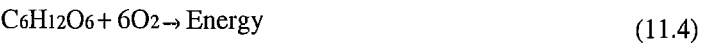
Correcting for atomic masses of C and N, 0.775 g N can oxidise 1.0 g of C, but this is only 53% as efficient as C oxidation under aerobic conditions. The NO₃ reduction under anaerobic conditions compared to C oxidised under aerobic condition is 1.473 g NO₃ compared to 1 g C.

To determine the amount of oxygen the nitrification process requires, the oxidation of NH₄ to NO₃ by *Nitrosomonas* and *Nitrobacter* can be summarised in Equation (11.3).



Equation (11.3) specifies that two moles of O₂ are required for every mole of NH₄ oxidised. In mass terms this represents 64 g of oxygen for every 14 g of N (4.57:1).

The oxygen requirements for C consumption can be seen from Equation (11.4) to be 6 moles of O₂ for 1 mole of glucose. On a C to O mass basis this represents 1 g C for every 2.66 g O.



11.8 Diffusion parameters

The diffusional constants used in CaNS-Eff are given in Table 11.35, based on data from Bolz and Tave (1976) and Wild (1981).

Table 11.35 Diffusional constants for dissolved components.

Material	Diffusional constant m ⁻² s ⁻¹
NH ₄	1.76E-9
Dissolved DFE OM high C:N (based on sucrose)	4.5E-10
Dissolved DFE OM low C:N (based on acetic acid & phenol)	8.6E-10
NO ₃	1.92E-9

For inter-layer diffusion, the distance that differences in concentration are considered to occur over is taken from the mid-point of one layer to the mid-point of the adjacent layer.

For intra-layer diffusion between micropore and mesopore domains the average distance between the two domains is not as intuitively obvious. In this instance, the distance used was based on the radius of the idealised cylindrical pore which is a function of the current soil water tension. The relationship between the radius of the idealised pore and the percent saturation in the mesopore domain was fitted with an

exponential curve and this relationship was implemented in CaNS-Eff to determine the typical distance to use for intra-layer diffusion.

11.9 Pasture sub-model parameters

Data for the estimation of foliage:root biomass ratio, C and N concentrations, root activity and translocation rates are summarised from a review of ryegrass-clover pastures by Brier and Ledgard (1998).

11.9.1 Foliage:root biomass ratio

Root biomass varies with species, time of year, stage of growth, N supply and soil moisture conditions (Garwood, 1967a; Garwood, 1967b; Garwood, 1967c). As the pasture in CaNS-Eff is considered to have both white clover (*Trifolium repens* L.) and perennial ryegrass (*Lolium perenne* L.) in the sward it is necessary to determine plant parameters for both of these species.

The foliage:root ratio presented in Table 11.36 is based on work by Harris (1994) and Pinxterhuis (unpublished). Harris (1994) measured root biomass to 7 cm depth and Pinxterhuis to 5 cm depth. From studies by Evans (1978), Williams *et al.* (1989), Garwood (1967a), and Matthew (1992) the measurements have been adjusted to total root biomass by assuming that Harris measured 60% (down to 7 cm depth) and Pinxterhuis measured 55% (down to 5 cm depth) of the total root biomass.

Table 11.36 Monthly foliage:root ratios for white clover under rotational grazed dairy farming. In this analysis, clover stolons have been included as part of the foliage biomass.

Month	Foliage:root ratio
January	2.41
February	2.21
March	2.19
April	2.09
May	1.93
June	2.02
July	1.97
August	2.02
September	2.00
October	2.09
November	2.16
December	2.74

While many studies report seasonal foliage biomass measurements, few have concurrently determined the root biomass. Francis *et al.* (1992) measured 4.7 to 6.3 t dry matter (DM) ha⁻¹ under a ryegrass-white clover sward. Gibbs (1986) summarised nine studies where ryegrass root mass had been measured and this had a range of 1.94 to 19.84 t DM ha⁻¹. The only consistent finding was that 60-80% of the total root mass was in the upper 0-150 mm soil depth. The best estimate as given in Table 11.37 is based mainly on the work of Matthew (1992) and Garwood (1967c).

Table 11.37 Monthly foliage:root ratios for ryegrass under rotational grazed dairy farming.

Month	Foliage:root ratio
January	0.76
February	0.86
March	0.88
April	0.81
May	0.79
June	0.81
July	0.86
August	0.86
September	0.82
October	0.78
November	0.75
December	0.74

11.9.2 C:N ratio of clover and ryegrass foliage and roots

The total amount of C present in grass and clover roots and foliage remains fairly constant throughout the year (Crush, J., 1998, pers. comm.), although the proportions of structural and non-structural C in the various components may vary (Care, D., 1998, pers. comm.). Relevant literature values are summarised in Table 11.38.

Table 11.38 C concentrations in roots and foliage of plants.

Reference	Basis of measurement	Plant type	% C
<u>Overseas studies</u>			
Kirchmann (1988)	DM	White clover - foliage	33.1
		- roots	39.8
Whitehead (1995)	Ash free organic matter	Grass and clover roots	48-49
Whitehead <i>et al.</i> (1979)	DM	Ryegrass roots	33.6
	Ash free organic matter		50.1
<u>New Zealand studies</u>			
D. Stewart, (pers. comm.)	DM - Ti corrected*	High Country - mixed foliage	42
		- mixed roots	46
		Low Country - mixed foliage	40
		- mixed roots	46.5
Saggar <i>et al.</i> (1997)	DM	Mixed foliage	37.8
		Mixed roots	33.7
Buwalda and Goh (1982)	DM	Ryegrass foliage	38-42.3

* DM -Ti measurement corrected for soil contamination from titanium measurement

To determine the C:N ratio of various components it has been assumed that the ryegrass and clover leaves both have constant 40% C and the roots have 45% C. Based on N herbage data from field measurements at Number 2 Dairy, Dairying Research Corporation, Hamilton (Ledgard, unpublished), the seasonal C:N ratios are given in Table 11.39.

Table 11.39 Monthly C:N ratios for white clover and ryegrass foliage.

Month	White clover foliage*	Ryegrass foliage
January	9.0	13.9
February	9.3	13.1
March	8.6	12.2
April	8.4	11.7
May	8.6	11.6
June	8.8	11.7
July	9.0	11.6
August	8.7	11.3
September	8.1	11.1
October	8.1	11.9
November	8.6	13.3
December	8.7	14.8

* Stolons have not been included in the foliage C:N ratio. Their C:N ratio is estimated to be between that of roots and foliage and to be approximately 18.

Time series data on the C:N ratio of plant roots are scarce, though reasonable amounts of data exist for single point measurements, which are summarised in Table 11.40.

Table 11.40 N concentrations in plant roots.

References	Basis of measurement	Species	% N
Francis <i>et al.</i> (1992)	DM	Ryegrass-white clover	1.7-2.3
Whitehead <i>et al.</i> (1990)	DM	Ryegrass	1.5
Ledgard <i>et al.</i> (1990)	DM	White clover	2.2
Kirchmann (1988)	DM	White clover	2.32

It has generally been observed that N concentration of roots decreased during spring and summer, and increased during the autumn to reach a maximum in mid-winter; this pattern mirrors the same trend as found in N concentrations in foliage. Based on this and a C concentration in roots of 45%, the monthly C:N ratio of white clover and ryegrass roots is given in Table 11.41.

Table 11.41 Monthly C:N ratios for white clover and ryegrass roots.

Month	White clover roots	Ryegrass roots
January	21.7	37.6
February	22.5	35.4
March	20.8	33.0
April	20.3	31.6
May	20.8	31.4
June	21.3	31.6
July	21.7	31.4
August	21.0	30.5
September	19.6	30.0
October	19.6	32.2
November	20.8	35.9
December	21.0	40.0

11.9.3 Tolerance of C:N ratio about optimum

While it appears that C concentrations remain fairly stable, (\pm 6-8%), N concentrations are more variable between seasons and environmental conditions. Based on measured N fluctuations from pasture trials, (Ledgard, unpublished), this would suggest a tolerance range for C:N ratio of -15% to +20%, occurring at transitional seasonal times of spring/summer and summer/autumn.

11.9.4 Root activity data

The work by Matthew (1992), Wedderburn (unpublished), and Garwood (1967a) provides good information for the root activity at various depths for ryegrass throughout the year, as given in Table 11.42.

Table 11.42 % of root activity at different depths for ryegrass.

Day of year	0-7 cm	7-30 cm	30-60 cm	60 cm +
15	57	28	11	4
43	58	30	9	3
74	60	30	8	2
104	65	29	6	0
135	69	28	3	0
165	69	31	0	0
196	69	31	0	0
227	69	31	0	0
257	65	33	2	0
288	59	32	8	1
318	54	29	14	3
349	50	27	16	7

11.9.5 Translocation of C and N

In a grazed pasture, there appear to be two different phases of translocation: the process that occurs during regular growth, and the process that commences immediately after defoliation when the plant remobilises reserves in order to re-establish photosynthetically active material to continue growth.

Parsons *et al.* (1983) measured a maximum gross photosynthetic uptake of 143 kg of C ha⁻¹ day⁻¹ in a grazed ryegrass pasture, while Deinum (1985) suggested that up to 200 kg of C ha⁻¹ day⁻¹ is a feasible maximum for a closed canopy. Parsons and Robson (1981) measured that approximately 10% of ¹⁴C applied to foliage was recovered from roots, and estimated that another 10% was exported to meet root respiration demands. Deinum (1985) argued that 27.5% of the daily photosynthesised C needs to be transferred to the roots for root turnover and respiration. This figure agrees well with the work of Saggar *et al.* (1997), which showed 34.5% transfer of annual assimilated C into roots in a low fertility pasture and 25.5% in a high fertility system. The results would mean that up to 55 kg of C ha⁻¹ day⁻¹ can be transferred to the below-ground part of the plant.

Using a pasture mass of 3000 kg DM ha⁻¹ and a 40% C content, the transfer rate of foliage-C to root-C, over 12 hours of sunlight, would be:

$$\text{Foliage to root C transfer rate: } 1.06 \mu\text{g of foliage C g of foliage}^{-1} \text{ s}^{-1}$$

The reverse flow from roots to foliage after cutting is limited by the amount of soluble carbohydrate reserves present in the roots and the nutrient status of the soil (Ourry *et al.*, 1994). During two days of regrowth following defoliation, the concentration of soluble carbohydrate fell from 15% to 6% in the stubble (as % of dry weight of plant) and only from 4% to 2% in the roots. This transfer appeared to cease after the first two days. For a pasture, assuming 4000 kg ha⁻¹ DM in root material, with a 50% reduction of soluble carbohydrate from 4 to 2% over a two day period, with 45% total C in root DM, the transfer rate of C from root to shoot would be:

$$\text{Root C to foliage C transfer rate: } 0.26 \mu\text{g of root C g root C}^{-1} \text{ s}^{-1}$$

Transfer of N from foliage to roots has been reported by Whitehead and Lockyer (1987), and Lockyer and Whitehead (1986, 1987). They measured the movement of atmospheric NH₃ absorbed by leaves and transported down to the roots at very high atmospheric concentrations, at adequate and low soil N levels. The total plant N taken up by atmospheric sources over 33 days growth varied between 4% at high levels to 77% at extremely low levels. Based on a growth rate of 100 kg DM ha⁻¹ day⁻¹, 16 hour adsorption period, 3000 kg DM ha⁻¹ of standing biomass, root growth at 20% of shoot growth, 3% N in foliage, 1.5% N in roots and 4% of the root-N being derived from foliage, the average N transfer from shoot to roots would be:

$$\text{Foliage to root N transfer rate: } 2.3 \text{ E } -2 \mu\text{g foliage N g foliage N}^{-1} \text{ s}^{-1}$$

For a ryegrass sward with a non-limiting nutrient supply under ideal weather conditions, growth rates of 100 kg DM ha⁻¹ day⁻¹ are achievable in the Waikato. Based on 3% pasture-N, this would require 3 kg N ha⁻¹ day⁻¹ to be translocated from 4000 kg DM root mass at 1.5% N over a 24 hour period. This represents an N transfer rate during normal growth of:

$$\text{Root to foliage N transfer rate: } 0.6 \mu\text{g root N g root N}^{-1} \text{ s}^{-1}$$

Remobilisation of N reserves after defoliation is an important process and considerable work has been done on it by Ourry *et al.* (1994). Their work suggested that for the first six days following defoliation nearly all the N came from roots and stubble. In this time 25% of the root total N supply at harvest was translocated in the first two days. Using these data the maximum rate of N remobilised after defoliation for two days would be:

$$\text{Root to foliage N transfer (after defoliation): } 0.7 \mu\text{g root N g root N}^{-1} \text{ s}^{-1}$$

This value agrees well with the above value for normal growth.

As clover has a different foliage:root ratio and has the ability to fix N, the transfer rate of root-N to foliage N is higher. Assuming that white clover at 70 kg DM ha⁻¹ day⁻¹ at 4.8% N requires 3.36 kg N ha⁻¹ day⁻¹ to be transferred, and based on 700 kg DM ha⁻¹ of root mass at 2% N, the daily average transfer rate of total N in clover would be:

$$\text{Clover root : foliage N transfer rate : } 2.8 \mu\text{g root N g root N}^{-1} \text{ s}^{-1}$$

11.9.6 Root uptake parameters

Work by Lycklama (1963) on the uptake of NH₄ and NO₃ by ryegrass suggests that the maximum rate of NH₄ uptake by the roots is 2.25E-8 g N g root-C⁻¹ s⁻¹ with a K_m of 0.56 μg N l⁻¹. The equivalent data from the same author for NO₃ was 1.56E-8 g N g root-C⁻¹ s⁻¹ with a K_m of 0.46 μg N l⁻¹. McGill *et al.* (1981) used values of 5.1E-8 g N g root-C⁻¹ s⁻¹ for V_{max} for the NH₄ uptake by the roots with a K_m of 0.34 μg N l⁻¹ for the first Michaelis-Menten expression and 2.55E-7 g N g root-C⁻¹ s⁻¹ and 42 μg N l⁻¹ for the second Michaelis-Menten factor. They used the same V_{max} value as for the NH₄ but a K_m value of 0.42 μg N l⁻¹ to describe the nitrate uptake kinetics. The values used in CaNS-Eff are based on Lycklama (1963) for nitrate, but slightly lower values for NH₄ to allow for a double Michaelis-Menten expression as suggested by McGill *et al.* (1981). Values used in CaNS-Eff are given in Table 11.43.

Table 11.43 Michaelis-Menten uptake kinetic values for root uptake.

	V _{max} g N g root-C ⁻¹ s ⁻¹		K _m mg N l ⁻¹	
	NH ₄	NO ₃	NH ₄	NO ₃
First MM	1.3E-8	1.56E-8	0.56	0.46
Second MM	1.3E-7	N/A	42	N/A

11.9.7 Root respiration rate

Parsons and Robson (1981) estimated that 50% of the C that is exported to the roots is lost as respiration. Based on 55 kg of C being translocated to the roots and 4000 kg ha⁻¹ of root DM material containing 45% total C, this results in a respiration rate of 1.77E-7 g C g root-C s⁻¹. This agrees reasonably well with the rate given by McGill *et al.* (1981) of 2.3E-8 g C g root-C s⁻¹ as the maximum root respiration rate. A rate of 1.0E-8 g C g root-C s⁻¹ was used as the maximum respiration rate in CaNS-Eff.

11.9.8 Root exudation

Newman (1985) reviewing data on root rhizodeposition, concluded that rates of C release were approximately 110 to 350 mg of C g⁻¹ of root produced. Using an average value of 300 mg of C g⁻¹ root and based on 4000 kg DM ha⁻¹ in the root system with 45% C, and that the root growth is 30 kg ha⁻¹ of root-C day⁻¹ this translates to an exudation rate of 1.08E-8 g exudation C g root-C⁻¹ s⁻¹. This value agrees

well with the value used in the PHOENIX model by McGill *et al.* (1981) of $9.26\text{E-}9$ g exudation C g root- $\text{C}^{-1} \text{s}^{-1}$.

Rhizodeposition material is considered to consist of 10-50% soluble C forms of simple monosaccharides, amino acids and organic acids and 50-90% as insoluble mucilages, sloughed-off cortical cells and dead root hairs (Darrah, 1997). The C:N ratio of this material was estimated to be 45.

11.9.9 Temperature effect on root activity

The temperature effect on root activity is based on McGill *et al.* (1981) and Luxmoore and Stolzy (1972) as given in Figure 11.3.

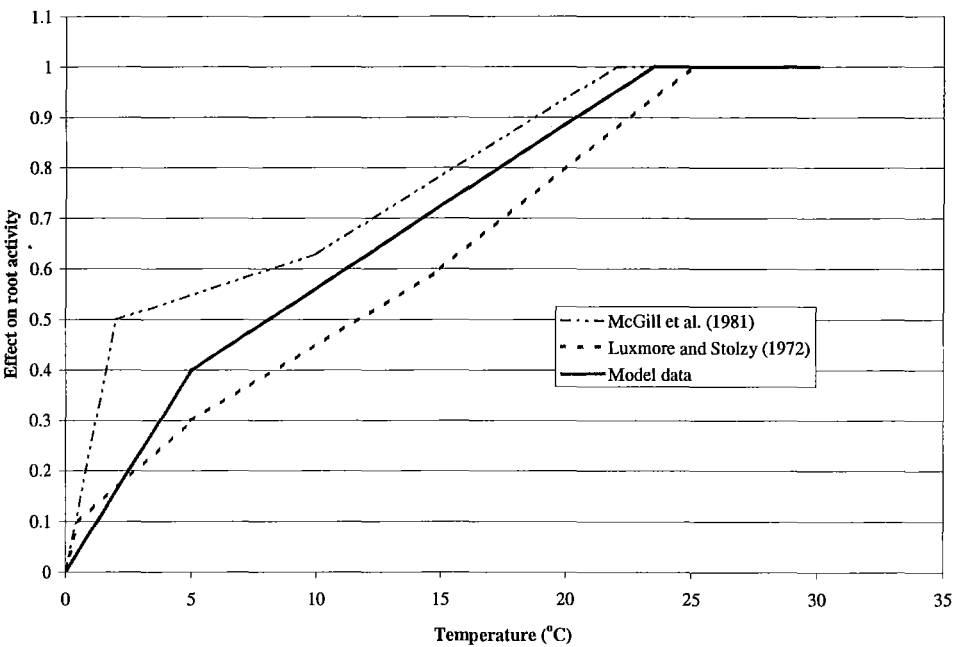


Figure 11.3 Temperature effect on root activity (McGill *et al.* 1981; Luxmore and Stolzy, 1972).

11.9.10 Water content effect on root activity

Following McGill *et al.* (1981) the moisture effect on root activity is given in Figure 11.4.

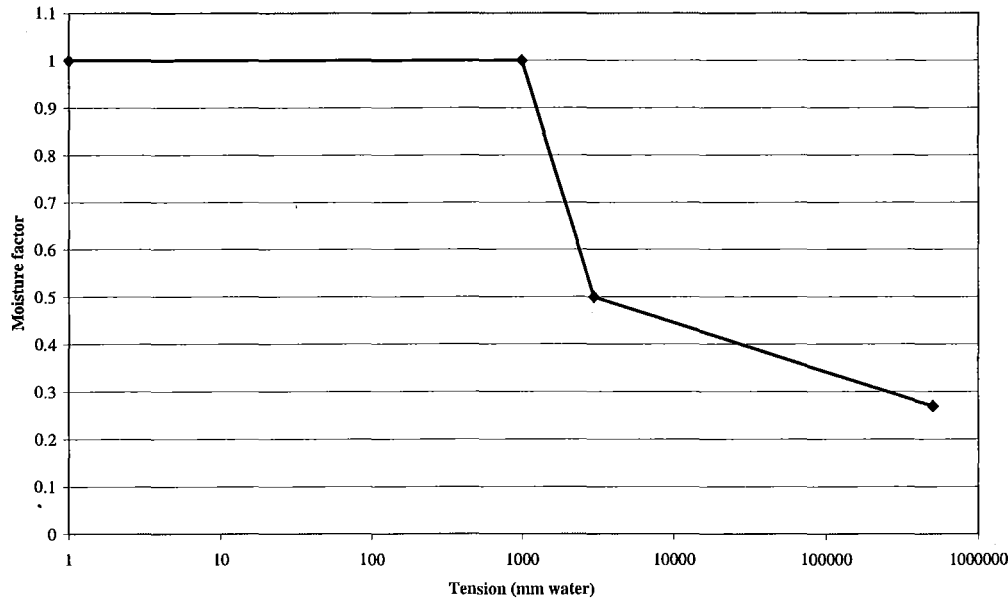


Figure 11.4 Soil water content effect on root activity (McGill *et al.* 1981).

11.9.11 Root turnover

Matthew (1992) measured root activity and concluded that root life span probably averages 215 days, corresponding to a turnover rate of $5.4\text{E-}8\text{ s}^{-1}$. This is in good agreement with the root turnover factor used in the PHOENIX model (McGill *et al.*, 1981) of $1.74\text{E-}8\text{ s}^{-1}$. The higher value of $5.4\text{E-}8\text{ s}^{-1}$ was used as this was measured under New Zealand conditions.

11.9.12 Miscellaneous pasture parameters

The amount of standing biomass left in the stubble after the foliage has been cut was estimated to be 825 kg DM ha⁻¹. Assuming that the C concentration is 40%, this represents 330 kg C ha⁻¹ as the standing biomass-C after cutting.

11.10 Gas sub-model

The gas model as described in Section 7.10 requires Van der Waals gas constants (Masterson and Slowinski, 1973) for each of the state gases tracked, as given in Table 11.44.

Table 11.44 Van der Waals gas constants for gases modelled.

Gas	Van der Waals A constant (l ² atm. mol ⁻²)	Van der Waals B constant (l ² atm. mol ⁻²)	Atomic mass unit
O ₂	1.36	0.032	32
CO ₂	3.59	0.043	44
N ₂	1.39	0.039	14
Air	1.40	0.039	90

The binary gaseous diffusion coefficient in free air used for oxygen is 0.206 cm² s⁻¹ and is 0.164 cm² s⁻¹ for carbon dioxide.

11.10.1 Soil tension versus oxygen concentration

Assuming that the atmospheric concentration of O₂ is approximately 330 g m⁻³ (Jury *et al.*, 1991), and using the soil data from the topsoil layer to determine the pore volume at various tensions, the relationship between soil tension to mass of oxygen in a soil layer was derived (Figure 11.5).

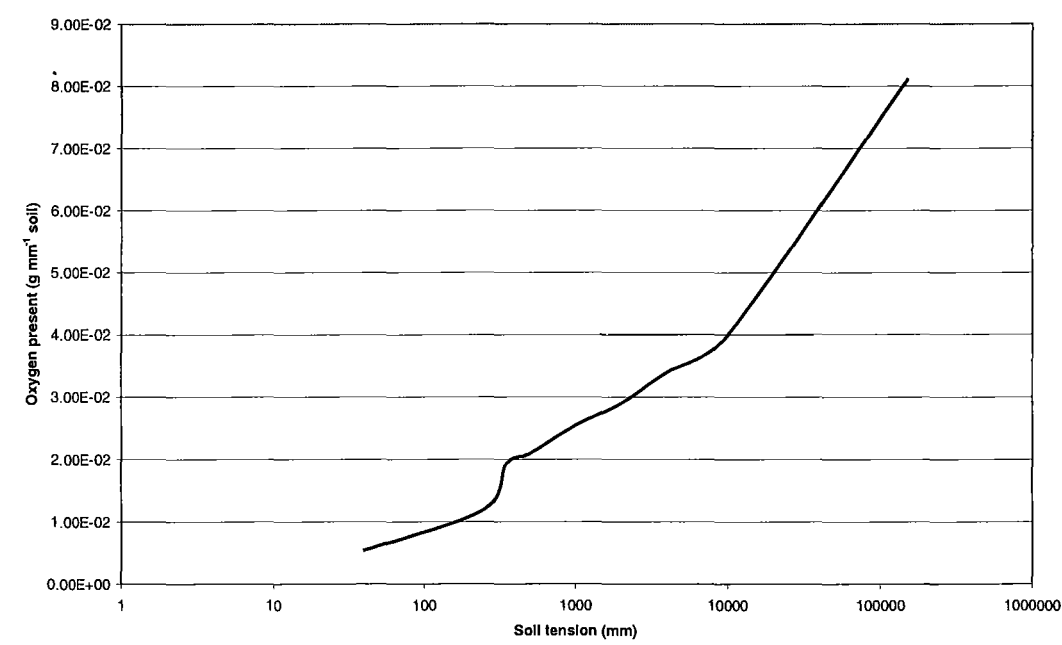


Figure 11.5 Soil tension versus mass of oxygen mm⁻¹ depth of soil.

11.11 Conclusions

The full parameter set used for simulating the DFE-irrigation onto the conventionally drained lysimeters has been presented. The parameters chosen should be considered as “best initial estimates” based on experimental work, published literature values and previous model studies, as they have not been adjusted to our data set, nor to the CaNS-Eff model.

11.12 References

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Chapter Twelve

Soil water dynamics: simulated versus measured

The objective of this Chapter is to:

Compare the soil water drainage and soil water contents simulated with CaNS-Eff with the measured data in the conventionally drained DFE-irrigated lysimeters

12.1 Introduction

The purpose of the following three Chapters is to check the adequacy of CaNS-Eff to simulate the hydrology and the fate of C and N from DFE applied onto the land. The input parameters used (Chapters 9 and 11) are “best estimates” based on measured field data, experimental work, literature values and other published model studies, but no sensitivity analysis or calibration has been undertaken at this initial testing stage. This test is thus rather an extended verification exercise than a validation of CaNS-Eff. A sensitivity analysis to identify critical parameters can be undertaken once the verification exercise has been completed successfully. These critical model parameters can subsequently be calibrated, and the model’s output validated against an independent data set. The sensitivity analysis, calibration of critical parameters and validation of CaNS-Eff are outside the scope of this thesis.

The soil water dynamics are a key component of any soil-based process model. The soil water fluxes control the movement of nutrients within the soil and their availability for transformation and uptake. The soil water status in a layer strongly impacts on all biological and chemical transformations in that layer. Thus, it is essential for the simulation of realistic nutrient leaching losses that the simulated hydrological conditions are in good agreement with measured data.

This Chapter presents data on the CaNS-Eff simulated soil water conditions and drainage volumes, for the conventionally drained DFE-irrigated lysimeters (0 treatment). Simulated values of weekly drainage volumes are compared to measured replicated ($n=3$) data over a 42 month period from September 1992 to March 1996. The simulated soil water contents at various depths are also compared to measured values over a 29 month period from September 1992 to February 1995.

12.2 Evaluation of model performance

Evaluating a simulation model’s performance is a subjective exercise that depends on the purpose and complexity of the model. How close the simulated values need to be to the measured values will depend on questions such as:

- how are the simulated values from the model to be used?
- what is the risk associated with the simulated values being wrong?
- how much natural variability should be expected in the values?
- what are the errors associated with the input and measured data?

Evaluating the performance of a simulation model is a judgement process rather than a deterministic decision. While statistical measures can be used in helping to evaluate a model’s performance, it is often the model user or intended recipient of a model’s output who must make their own judgement about whether they consider the model’s performance to be satisfactory for their purpose.

The difference between a measured value (y) and a simulated value (x) is termed the residual (d). The residuals can be either positive or negative; in an unbiased model their sum will tend to zero. The residual is made up of random and/or systematic errors. The random error or pure error is due to the difference

between replicated measurements and their mean, while the systematic error is due to the lack of fit of the model.

Following Whitmore (1991) and Greenwood *et al.* (1985), where methods are given for assessing the goodness of fit of computer simulation to measured soil and crop data, four statistical measures have been used in this study.

The first of these is the Students *t*-test (Equation 12.1), which is used to see if the simulated value is within the random error of the measurements. The test is carried out by comparing each simulated value, *x*, with the mean measurement, \bar{y} (MacBerthouex and Brown, 1994). The *t*-statistic is calculated as:

$$t = \frac{(\bar{y} - x)}{SE} = \frac{\bar{d}}{SE} \quad (12.1)$$

where:

SE = standard error of the mean measurement $\frac{\text{stdev}}{\sqrt{n}}$

\bar{y} = mean of the measurements

x = simulated value

n = number of replicates

stdev = sample standard deviation

Whitmore (1991) suggested that if the number of replicates is low then the *t*-test becomes a fairly easy test to pass. As an alternative method he suggested that the sum of the squares of the error in the measurements SSE (Equation 12.2) is subtracted from the sum of squares in the residuals RSS (Equation 12.3) which results in the sum of squares attributable to the lack of fit of the model (Equation 12.4):

$$SSE = \sum_{j=1}^N \sum_{i=1}^{n_j} (d_{ij} - \bar{d}_j)^2 = \sum_{j=1}^N \sum_{i=1}^{n_j} \left((y_{ij} - x_j) - (\bar{y}_j - x_j) \right)^2 \quad (12.2)$$

$$RSS = \sum_{j=1}^N \sum_{i=1}^{n_j} d_{ij}^2 = \sum_{j=1}^N \sum_{i=1}^{n_j} (y_{ij} - x_j)^2 \quad (12.3)$$

$$LOFIT = \sum_{j=1}^N n_j \bar{d}_j^2 = \sum_{j=1}^N n_j (\bar{y}_j - x_j)^2 \quad (12.4)$$

where:

N = number of experiments

n_j = number of replicates within each experiment

x_j = simulated value of the j^{th} experiment

y_{ij} = i^{th} measurement in the j^{th} experiment

\bar{y}_j = mean of the measurements in the j^{th} experiment

d_{ij} = deviation ($y_{ij} - x_j$)

\bar{d}_j = mean deviation ($\bar{y}_j - x_j$).

By dividing each of the sums of squares by its associated number of degrees of freedom, this results in a mean square (which is a variance). The relative sizes of the mean squares due to error and lack of fit can then be compared using the F-test. Where the lack of fit is significantly greater than the error, then the model could be improved.

The third measure is the size of the sum of the squares of the residuals compared to the total sum of squares in the data about their mean (Equation 12.5), which was used by Greenwood (1985) to evaluate the output from a crop growth model:

$$\% \text{ variance} = 100 \left(\text{RSS} / \sum_{i=1}^{N_i} \sum_{j=1}^{n_j} (y_{ij} - \bar{y})^2 \right) \quad (12.5)$$

where:

\bar{y} = mean of all the observations.

As a percentage this is analogous to the per cent variation in the data accounted for by the model; however it can exceed 100%. The disadvantage of this measure, as described by Whitmore (1991), is that it takes no account of replicated measurements, except to include all replicates in both sums of squares; some replicated measurements are bound to contain less experimental error than others.

The final measure is the parameters of a linear regression analysis between measured values (Y axis) and the simulated values (X axis) using SYSTAT 9 (SPSS Inc., Chicago, USA, 1996). If agreement between measured and simulated was perfect then the intercept of the linear regression line would be zero, the slope = 1.0 and $R^2 = 1.0$.

12.3 Results

12.3.1 Drainage volumes

The simulated drainage volumes have been summed over a period (typically weekly) to synchronise with measured drainage volumes ($n=183$) whenever a chemical analysis of leachate was undertaken. The cumulative measured and simulated drainage volumes are given in Figure 12.1.

Except for a short period at the beginning of 1993, the cumulative drainage volume is always within the 95% confidence interval (CI). The cumulative drainage volume simulated is always greater than that measured. However, by the end of the simulation period the simulated and the measured mean value are almost identical with only a 19 mm difference (0.5%). The simulated and measured drainage volumes on a six monthly basis are given in Table 12.1.

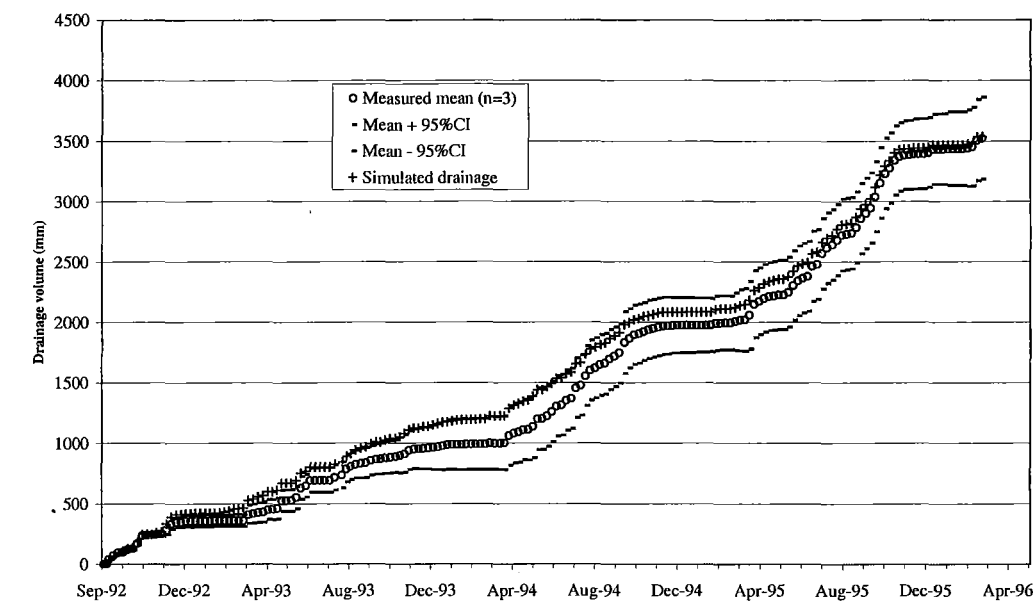


Figure 12.1 Simulated versus measured cumulative drainage volume for conventionally drained DFE-irrigated lysimeters. Mean \pm 95 % confidence interval (CI) shown for measured data.

Table 12.1 Simulated and measured drainage for six-month periods from September 1992 to March 1996.

Period	Simulated drainage volume (mm)	Measured mean drainage (mm)	Standard error of mean (mm)	Residual (Mea-Sim.) (mm)	Residual as % of mean (%)
September 1992 - February 1993	431	359	9	-72	20
March 1993 - August 1993	483	443	15	-40	9
September 1993 - February 1994	279	173	21	-106	61
March 1994 - August 1994	623	654	8	31	-5
September 1994 - February 1995	296	361	26	66	-18
March 1995 - August 1995	710	746	16	36	-5
September 1995 - March 1996	716	781	10	66	-8
TOTAL	3537	3518		19	1

Of the 183 simulation periods (Figure 12.2), 29% of the simulated drainage volumes were above and 27% below the boundary of the 95% CI, with 44% being within the CI.

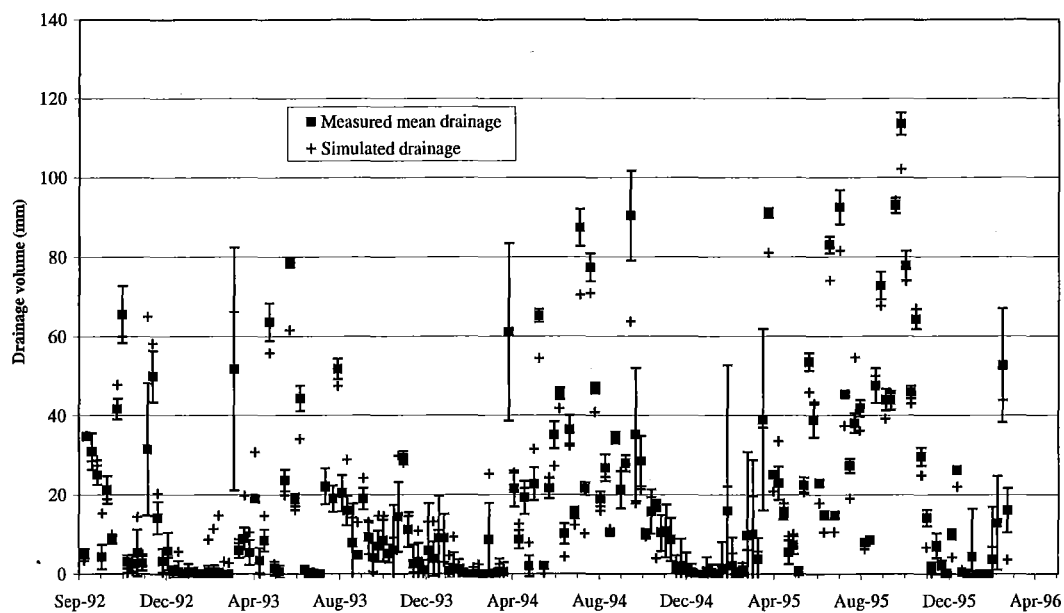


Figure 12.2 Simulated versus measured drainage volume with individual simulation periods for conventionally drained DFE-irrigated lysimeters. Mean \pm 95% CI data shown.

The simulated versus measured mean data are shown in Figure 12.3. The linear regression line suggests that the simulated values are under-estimated (coefficient of the linear regression equation = 1.02).

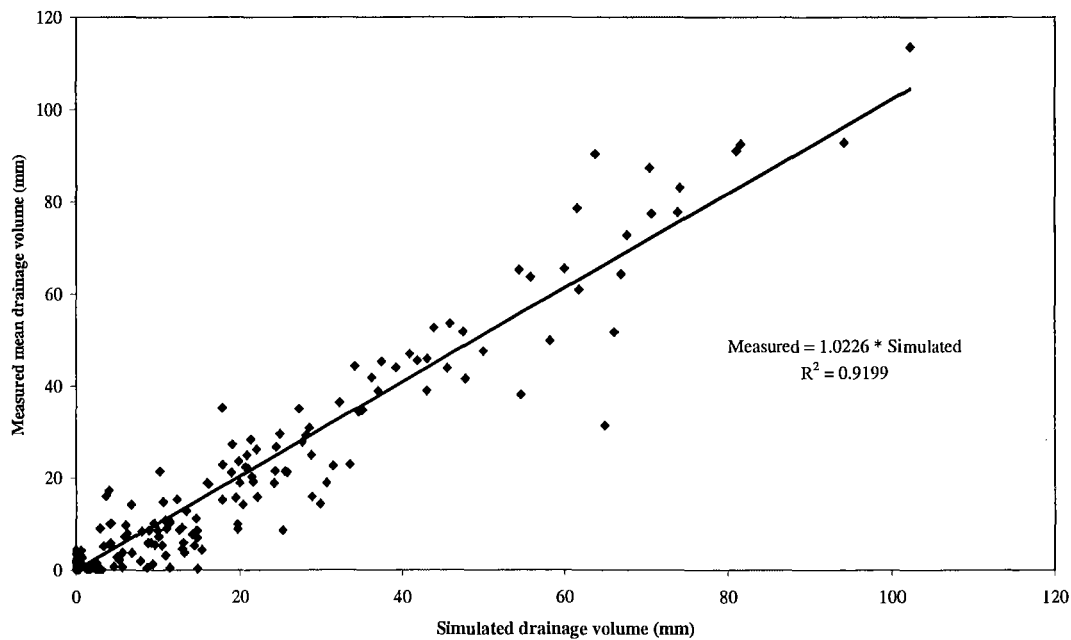


Figure 12.3 Simulated versus measured drainage volume for conventionally drained DFE-irrigated lysimeters. Linear regression equation forced through origin.

The plot of the residuals (measured - simulated) against the size of the actual drainage volume (Figure 12.4), shows that the model generally over-estimates drainage volumes above 20 mm, and below this value will tend to under-estimate.

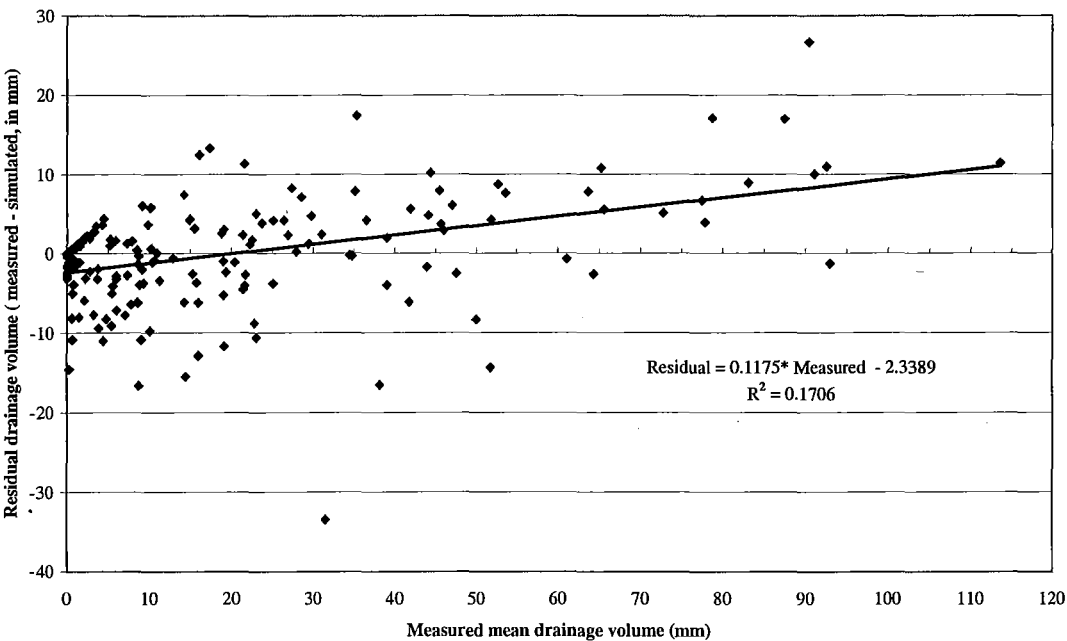


Figure 12.4 Measured mean drainage volume versus residual (measured - simulated) for conventionally drained DFE-irrigated lysimeters.

The statistical measures for evaluating the goodness of fit of the model (Whitmore, 1991) are presented in Table 12.2. The % variance (Greenwood *et al.*, 1985) was 9%.

Table 12.2 Statistical measures for goodness of fit of simulated versus measured drainage volumes for the conventionally drained DFE-irrigated lysimeters.

Residual sum of squares (RSS)	Mean sum of squares due to pure error (MSE)	Mean square due to lack of fit (MSLOFIT)	Ratio of lack of fit/pure error (MSLOFIT/MSE)
28108	6.73	139.3	20.7

12.3.2 Water contents within profile

Soil water contents were measured on 113 dates from September 1992 to February 1995 using a neutron probe (Troxler Neutron Probe Model 3320). Neutron probe counts were taken at depths of 5, 15, 25, 35, 45, 55 and 63 cm below the surface. Layer-specific calibration curves were derived from separate neutron probe access tubes in the field from where the lysimeters were collected, and the neutron counts determined over a range of soil water contents (Singleton, 1997).

As the probe integrates over a depth increment the data measured at 5 cm depth were compared to the 0-10 cm simulated soil water contents; similarly the 25 and 45 cm measured values were compared to simulated 20-25, and 45-50 cm soil layers. The 0-10 cm simulated soil moisture was obtained by depth averaging the first four computational soil layers (0-1, 1-2, 2-5, 5-10 cm) while the other two depths correspond directly to computational layers.

The soil water contents have been translated to a water filled pore space (WFPS) by dividing the water content by the total porosity for each layer. This translation enables the reader to gain an appreciation of the degree of wetness in the different soil layers. Figures 12.5 to 12.7 give the simulated versus measured data for the 0-10, 20-25 and 45-50 cm soil layers.

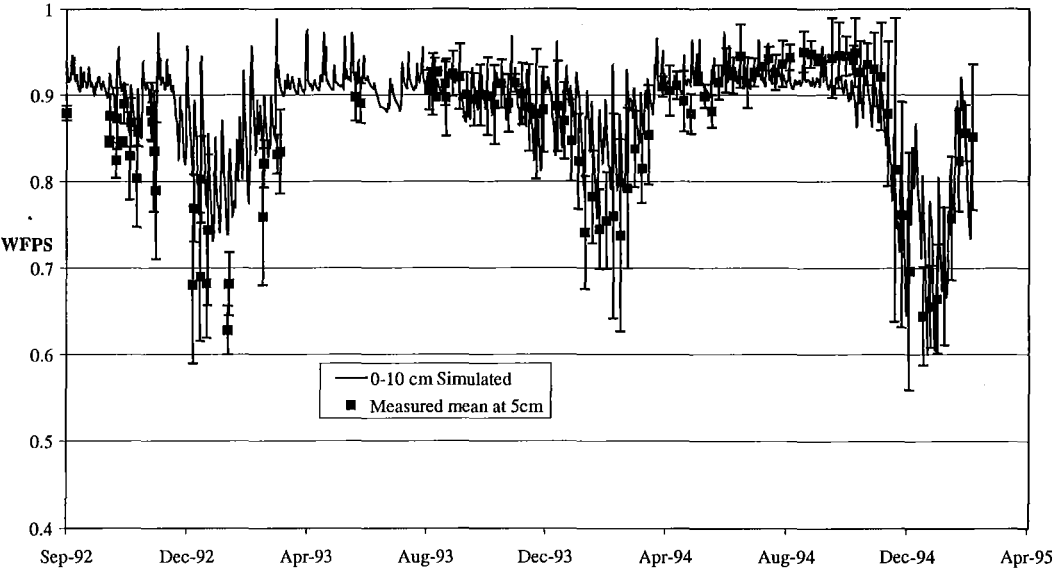


Figure 12.5 Simulated versus measured WFPS in the 0-10 cm soil layer. Measured values are mean values \pm 95% CI.

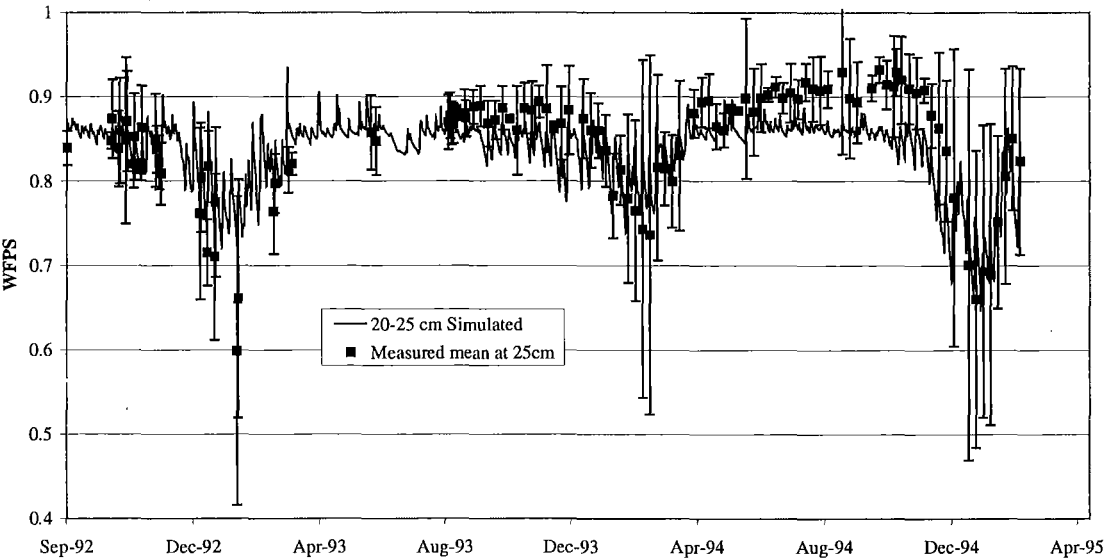


Figure 12.6 Simulated versus measured WFPS in the 20-25 cm soil layer. Measured values are mean values \pm 95% CI.

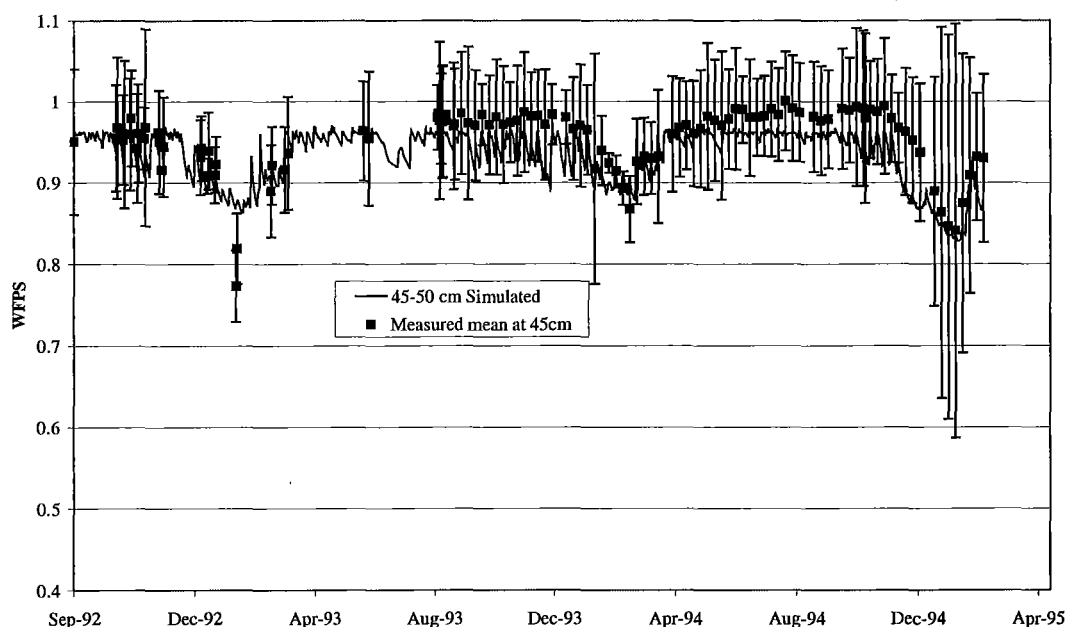


Figure 12.7 Simulated versus measured WFPS in the 45-50 cm soil layer. Measured values are mean values \pm 95 % CI.

The accuracy of the simulated WFPS increases with depth (Table 12.3), which also shows that over-estimation prevails in the 0-10 cm layer and under-estimation in the 20-25 cm layer.

Table 12.3: Accuracy of WFPS for various soil layers within the conventionally drained DFE-irrigated lysimeters.

Neutron probe depth	Soil computational layer	Simulated values greater than mean + 95% CI	Simulated values less than mean - 95% CI	Simulated values within limits
5 cm	0-10 cm	37%	8%	55%
25 cm	20-25 cm	5%	30%	65%
45 cm	45-50 cm	3%	8%	89%

The simulated versus the average measured WFPS is given in Figures 12.8 to 12.10 for the 0-10, 20-25 and 45-50 cm layers.

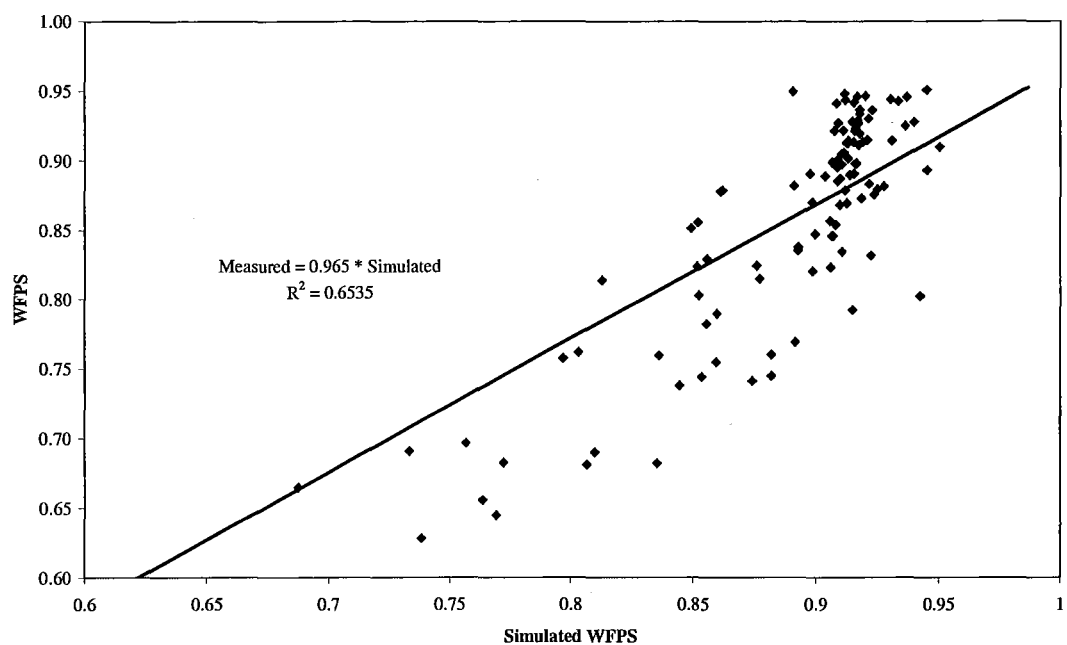


Figure 12.8 Simulated versus average measured WFPS in the 0-10 cm layer for conventionally drained DFE-irrigated lysimeters. Linear regression equation forced through origin.

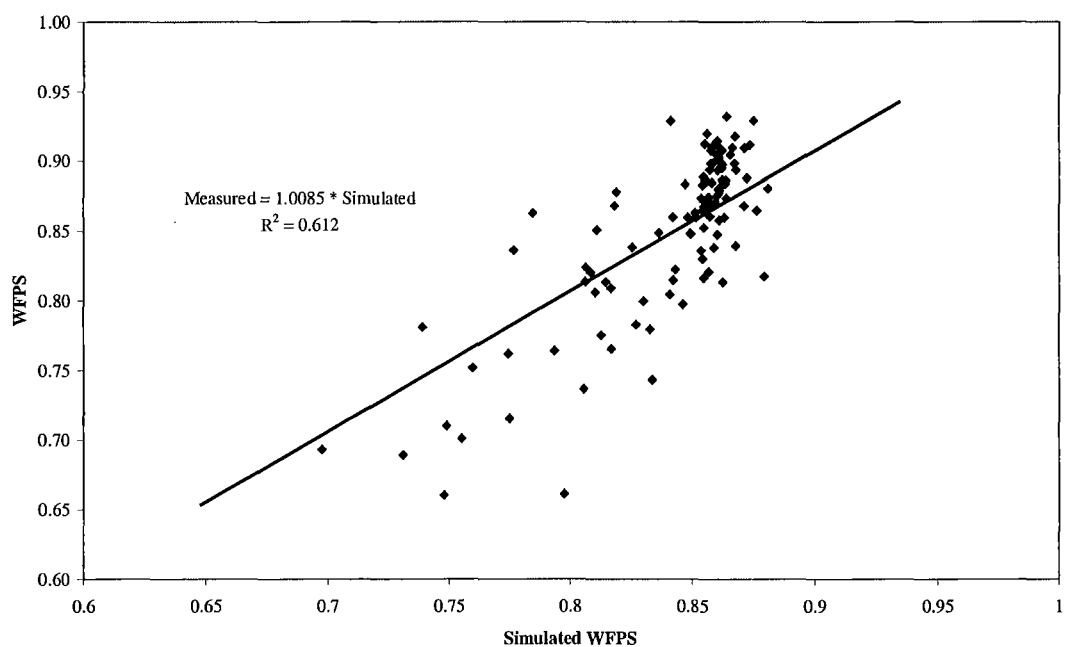


Figure 12.9 Simulated versus average measured WFPS in the 20-25 cm layer for conventionally drained DFE-irrigated lysimeters. Linear regression equation forced through origin.

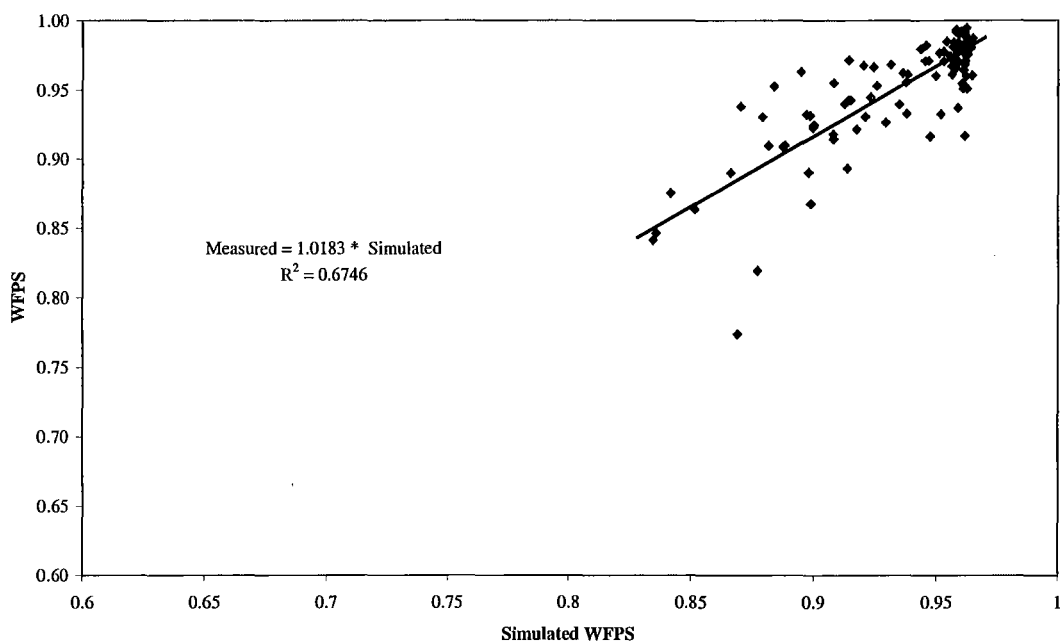


Figure 12.10 Simulated versus average measured WFPS in the 45-50 cm layer for conventionally drained DFE-irrigated lysimeters. Linear regression equation forced through origin.

Table 12.4 presents the statistical measures for the goodness of fit of the simulated WFPS values. The % variance (Greenwood *et al.*, 1985) for the three layers with increasing depth is 31.7, 24.9 and 74.8 %.

Table 12.4 Statistical measures for goodness of fit of simulated soil saturation in layers 0-10, 20-25 and 45-50 cm for the conventionally drained DFE-irrigated lysimeters.

Soil layer (cm)	Residual sum of squares (RSS)	Mean sum of squares due to pure error (MSE)	Mean square due to lack of fit (MSLOFIT)	Ratio of lack of fit/pure error (MSLOFIT/MSE)
0-10	1.15	4.82E-4	9.74E-3	20.2
20-25	0.74	8.87E-4	5.12E-3	5.77
45-50	0.49	1.07E-3	2.57E-3	2.40

12.4 Discussion

12.4.1 Drainage volume

Generally CaNS-Eff's performance in simulating the drainage volume was satisfactory and the agreement in the measured and simulated total cumulative drainage volume after 42 months was extremely good. It is recognised that the total cumulative volume masks periods of over- and under-estimation that are evident in the six-monthly total drainage data. The model's performance on the six-monthly basis was still satisfactory with six of the seven drainage volume residuals being less than 20%, and averaging 10%, of the measured mean cumulative drainage volume. In the one case where it was greater than 20%, the mean

cumulative drainage volume for the period was very low, 173 mm compared to a mean of 500 mm for the other three spring-summer periods. The variability in the measurements for this period ($CV = 20\%$) was the highest for all periods, which indicates greater uncertainty in the actual measurements.

The linear regression analysis (Figure 12.3) showed that CaNS-Eff was able to explain 92% of the variation in the measured mean data. The model was slightly under-estimating the drainage volume evident from the slope of this regression line (1.02). The CI of the slope of the regression included 1.0 which indicates perfect fit between measured and simulated values.

The residuals show a weak trend with drainage volume (Figure 12.4), where the smaller drainage volumes are under-estimated while the drainage volumes greater than 20 mm are generally over-estimated. While there were twice the number of small drainage volumes (121 versus 62) the drainage volume from the small events is only 20% of the total drainage volume. As was found in the initial hydrology model selection exercise (Chapter 9), the greatest residuals occurred during wetting-up events over summer and autumn.

The ratio of the MSLOFIT/MSE indicates that the error in the lack of fit of the simulated values was approximately 20 times greater than the pure error in the measured data, indicating that the model could be improved. This high ratio is more a function of the relatively small pure error in the measured drainage volumes from the three lysimeters, as opposed to a bad fit from the model. The lysimeters were located relatively close to each other and it could be argued were not truly independent, as they all received the same rainfall and were subject to the same potential evapotranspiration.

The residual variation between model and measurement is 9% of the variation of all measured data about their mean; therefore 91% of the variation in the measurement was explained by the model. On the basis of the *t*-test, 45% of the simulated values were within the range of the measured mean $\pm 95\%$ CI.

12.4.2 *Water contents within profile*

On an event basis, the accuracy of the simulated WFPS was better than that of the drainage volumes. For the three soil layers investigated, 55, 65, and 89% of the simulated WFPS levels were within the measured mean $\pm 95\%$ CI. As expected, there was a better fit deeper in the soil profile where there was less variation in the WFPS. The CI of the slope of the three regression lines (Figures 13.8 - 13.10) all included 1.0. The ratio MSLOFIT/MSE indicated that the model's performance improved with depth to a point where the lack of fit in the lower 45-50 cm layer was only 2.4 times greater than the pure error in the measurements.

12.5 Conclusions

As discussed in Section 12.2, describing the performance of a model is a subjective exercise depending on the purpose and complexity of a model. The parameters for the CaNS-Eff model have not been systematically calibrated but are “initial best estimates”. Accordingly, the purpose of this initial test is not to validate CaNS-Eff, but to ascertain the adequacy of the model to describe the fate of DFE applied onto the soil. While the ratio of the MSLOFIT/MSE indicates that CaNS-Eff could be improved upon, the accuracy of the cumulative six-monthly and total data, the slope and fit of the regression equations and the percentage variance would all allow us to conclude that for the purposes of this preliminary study, the simulated drainage volumes and soil water content can be considered satisfactory. A full systematic sensitivity analysis needs to be undertaken to fully quantify the impact that any errors in the simulated soil water conditions will have on the fate of the carbon and nitrogen from an organic effluent applied onto the soil.

12.6 References

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Chapter Thirteen

C and N leaching: simulated versus measured

The objective of this Chapter is to:

Compare the CaNS-Eff simulated C and N leaching to the measured data in the conventionally drained DFE-irrigated lysimeters

13.1 Introduction

The transport of nutrients in the water draining from an effluent application site is a major mechanism for the impact of the activity on the environment. The nutrients, once leached below the root zone, may either move sideways into surface water or move vertically into groundwater systems, where they may be diluted and move off-site.

This Chapter presents a comparison of simulated versus measured N and C leaching from the conventionally drained DFE-irrigation lysimeters (0 treatment). Nitrogen is leached as either inorganic N (ammonium and nitrate) or as organic N. In the model, three pools can contribute to leached organic C and N: particulate material contained in POM, or dissolved material in the DOMhighCN and DOMlowCN pools (Table 10.4).

Simulated and measured N leaching are compared over a 42 month period; from September 1992 to March 1996. This period covers three DFE-irrigation periods (Table 13.1) and a subsequent 10 month period when no DFE was applied.

Table 13.1 C and N loadings applied onto the lysimeters over the three years of DFE-irrigation.

Period of application	C loading (kg C ha ⁻¹)		N loading (kg N ha ⁻¹)	
	DFE	Pasture	DFE	Pasture
September 1992 to April 1993	5768	4830	510	341
August 1993 to April 1994	21661	----	1519	----
August 1994 to May 1995	9697	----	1554	----

Due to operational constraints, the organic component of the leachate could not be measured separately for each lysimeter during the whole experiment. Composite samples were used for the period from 4.6.1993 to 25.10.1994. To provide an estimate of the variation in a bulked sample, the average standard error as a fraction of the replicated mean was determined, and used as an estimate of the standard error of the bulked samples. The nitrate leaching data from one of the lysimeters during the period 8.1.1994 to 27.6.1995 was not included because of the nitrated effluent experiment conducted on that lysimeter, as reported in Chapter 7.

The measurement of C leaching from the lysimeters started in August 1993 and ran through to March 1996, a 31-month period. As with the organic N samples, the C samples were volumetrically bulked until November 1994 and the same method as for organic N was used to estimate a standard error during this period.

As the simulation results are based on uncalibrated parameters, and the absolute measured values were often low, a more sophisticated statistical analysis than the Students *t*-test (Equation 12.1) was not considered appropriate unless otherwise stated.

13.2 Effluent input

The concentrations of the particulate and dissolved C and the organic N and NH₄ are shown in Figures 13.1 and 13.2, respectively, to document how strongly the composition of the DFE changed over the three years of irrigation. In the first year of lysimeter operation, approximately 60% of the pasture clippings from each lysimeter were also returned. The C and N loadings over the four years of operation are summarised in Table 13.1.

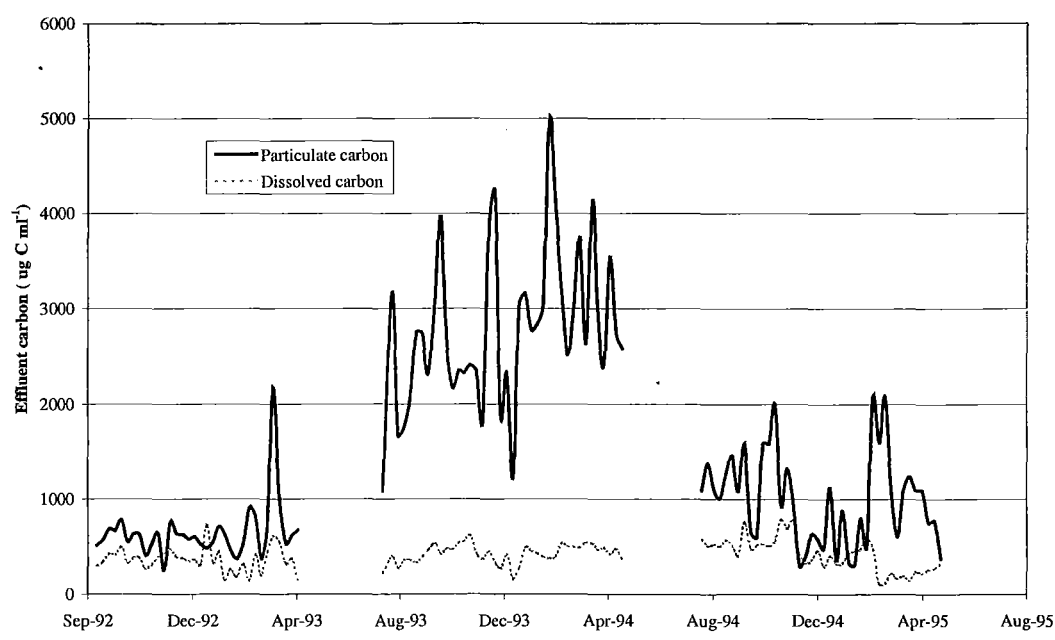


Figure 13.1 Concentration of particulate and dissolved C fractions during the three years of DFE-irrigation.

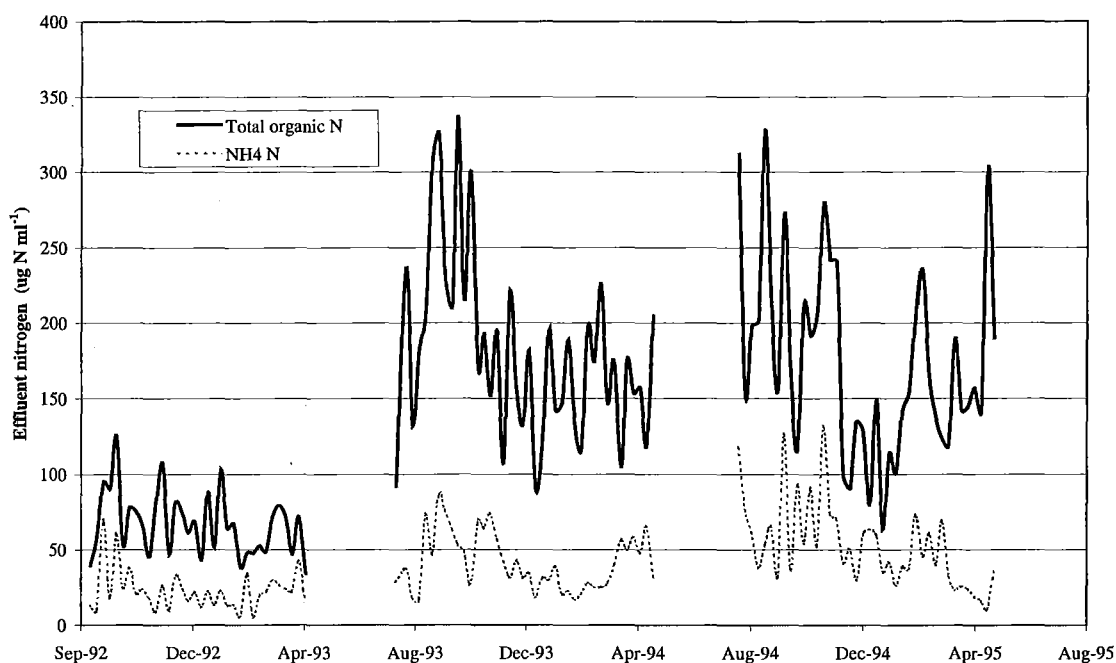


Figure 13.2 Concentration of organic N and $\text{NH}_4\text{-N}$ during the three years of DFE-irrigation.

13.3 Results

13.3.1 Nitrate leaching

The simulated cumulative nitrate leaching of only $4.7 \text{ g NO}_3\text{-N m}^{-2}$ over the 42 months of lysimeter operation is in very good agreement with the very low measured amount of $3.0 \text{ g NO}_3\text{-N m}^{-2}$ and is within the 95% CI (Figure 13.3).

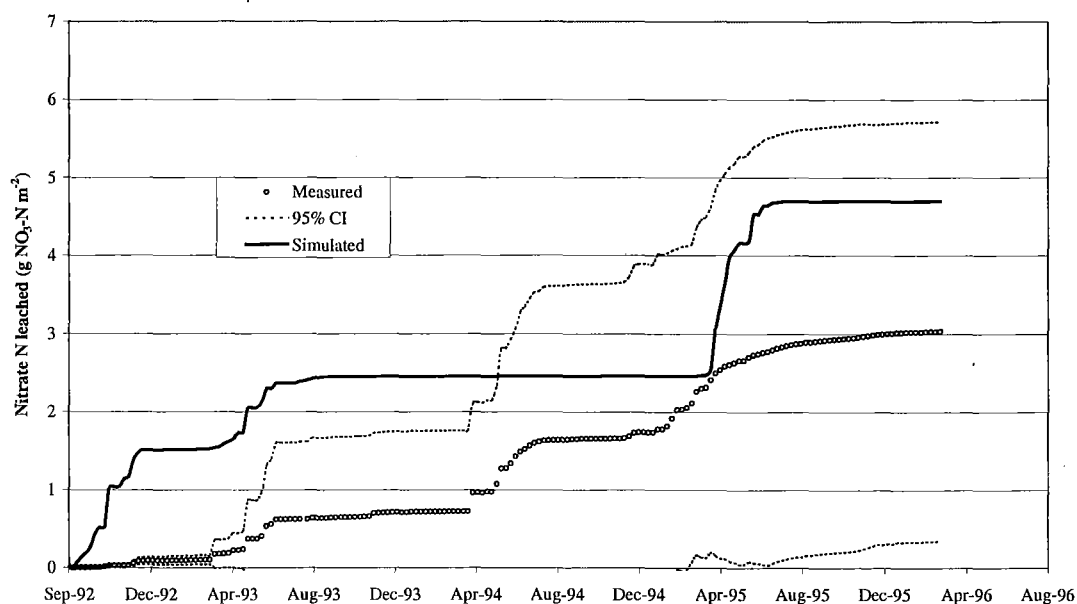


Figure 13.3 Simulated versus measured $\text{NO}_3\text{-N}$ leaching for the conventionally drained DFE-irrigated lysimeters from September 1992 to March 1996. Mean \pm 95% CI.

In terms of the temporal dynamics, CaNS-Eff correctly simulated the time and amounts of the autumn flush in 1993 but the timing was slightly late and the amount over-estimated in the autumn of 1995. In contrast to the measured leaching of 1.0 g NO₃-N m⁻², no leaching was simulated in the autumn of 1994.

13.3.2 Ammonium leaching

The simulated 2.7 g NH₄-N m⁻² leached during the 42-month period is in very good agreement with the very low measured amount of 2.5 g NH₄-N m⁻². However, as shown in Figure 13.4, the very good agreement of the cumulative amount results from an under-estimation until May 1995, followed by an over-estimation.

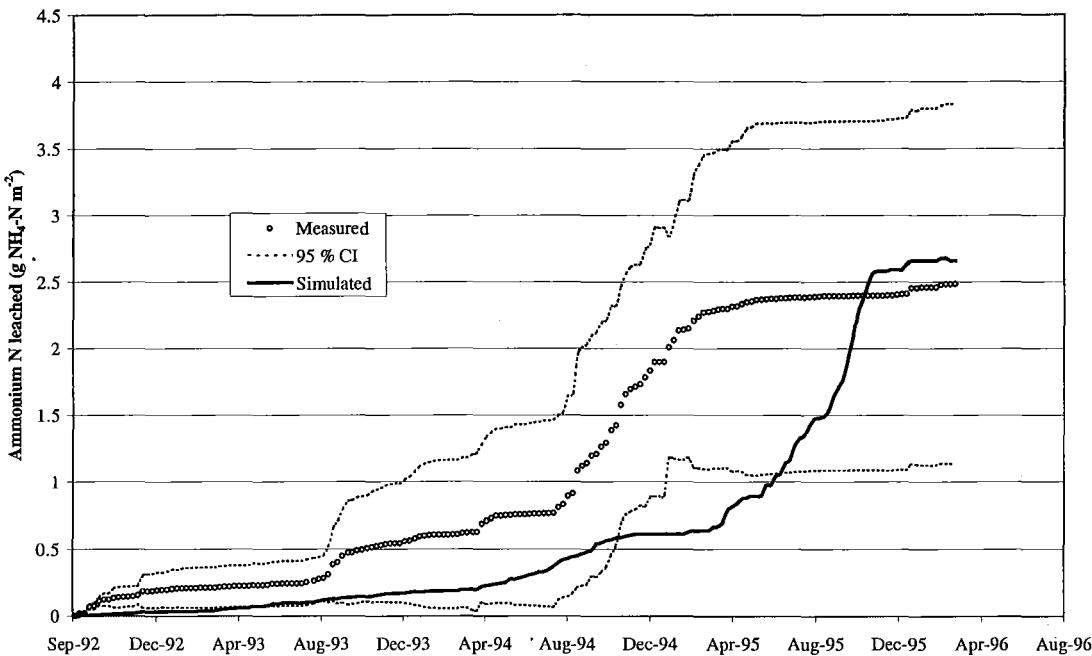


Figure 13.4 Simulated versus measured NH₄-N leaching for the conventionally drained DFE-irrigated lysimeters from September 1992 to March 1996. Mean \pm 95% CI.

13.3.3 Organic N leaching

Organic N is simulated in both dissolved and particulate fractions separately, but only the total amount was measured. Figure 13.5 shows the simulated versus measured total organic N leached over the 42-month period, while the simulated dissolved and particulate fractions are shown in Figure 13.6.

The simulated amount of 58.3 g total organic N m⁻² leached over the 42-month period over-estimated the measured amount of 24.3 g organic N m⁻², as seen in Figure 13.5. Over-estimation is apparent from autumn 1994 onwards, but a great part of the cumulative amount stems from the post-irrigation period. Less than 0.5 g organic-N m⁻² was actually measured after May 1995, whereas leaching of approximately 18 g organic N m⁻² was simulated. The over-estimation during this period is exclusively caused by dissolved organic N (Figure 13.6).

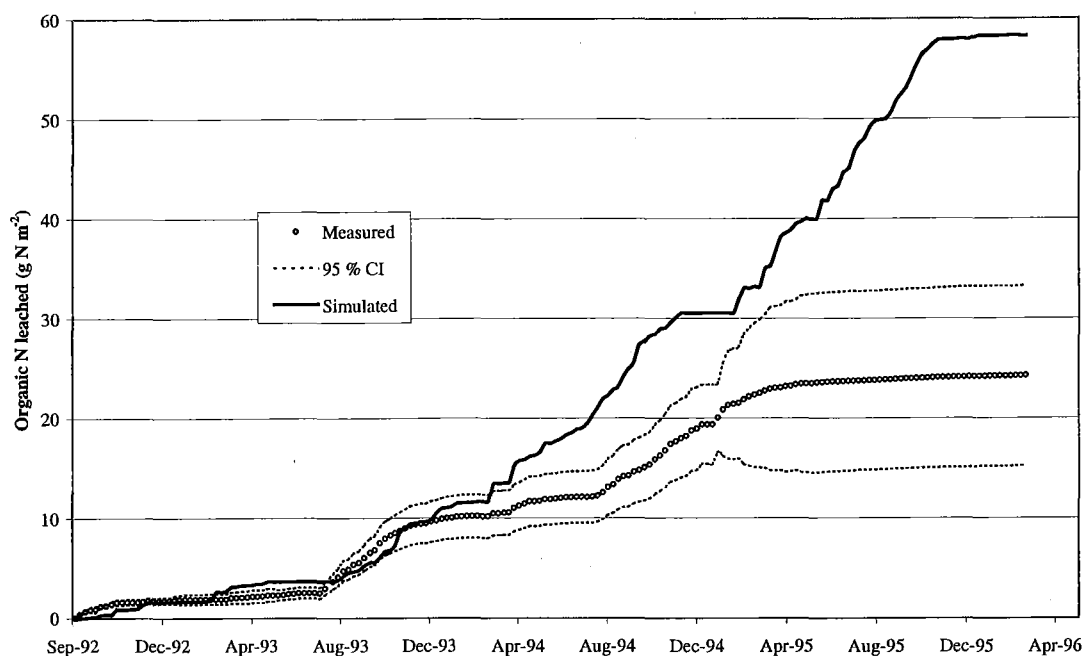


Figure 13.5 Simulated versus measured organic N leaching for the conventionally drained DFE-irrigated lysimeters from September 1992 to March 1996. Mean \pm 95 % CI.

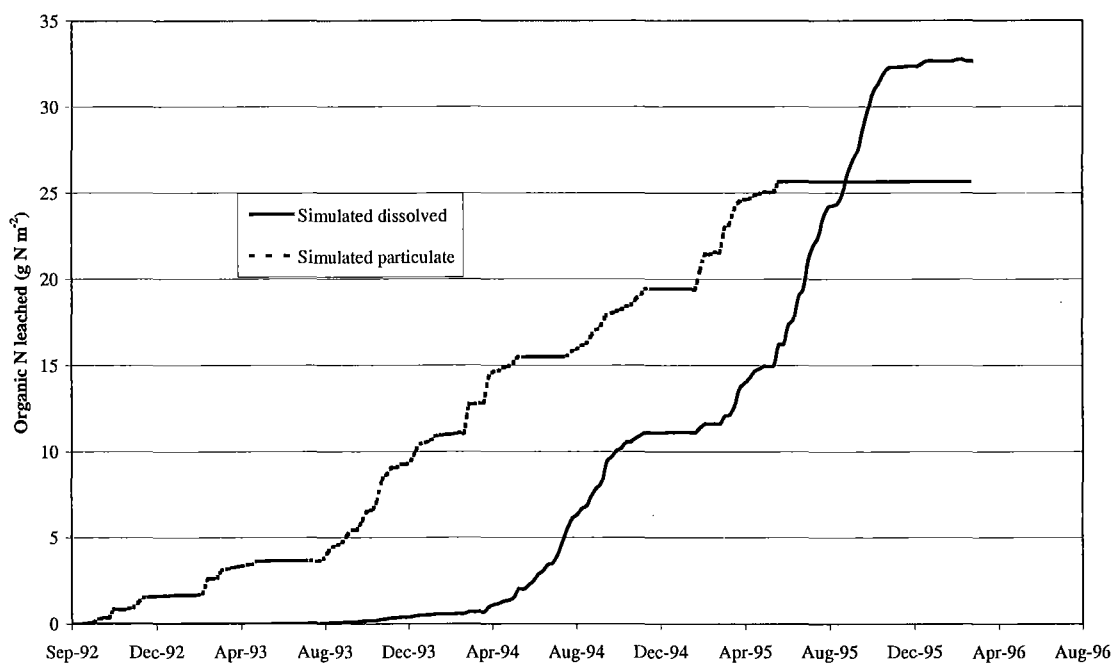


Figure 13.6 Simulated dissolved and particulate N leaching for the conventionally drained DFE-irrigated lysimeters from September 1992 to March 1996.

13.3.4 Particulate organic C leaching

The simulated cumulative leaching of particulate C of 305 g C m⁻² at the end of the 31-month period was within the 95% CI of the measured value of 224 g C m⁻² (Figure 13.7). A brief initial period of under-estimation was followed by a large over-estimation in autumn 1994, which resulted in the simulated total being temporarily outside the 95% CI. Cumulative values returned into the 95% CI during spring 1994 when leaching was greatly under-estimated.

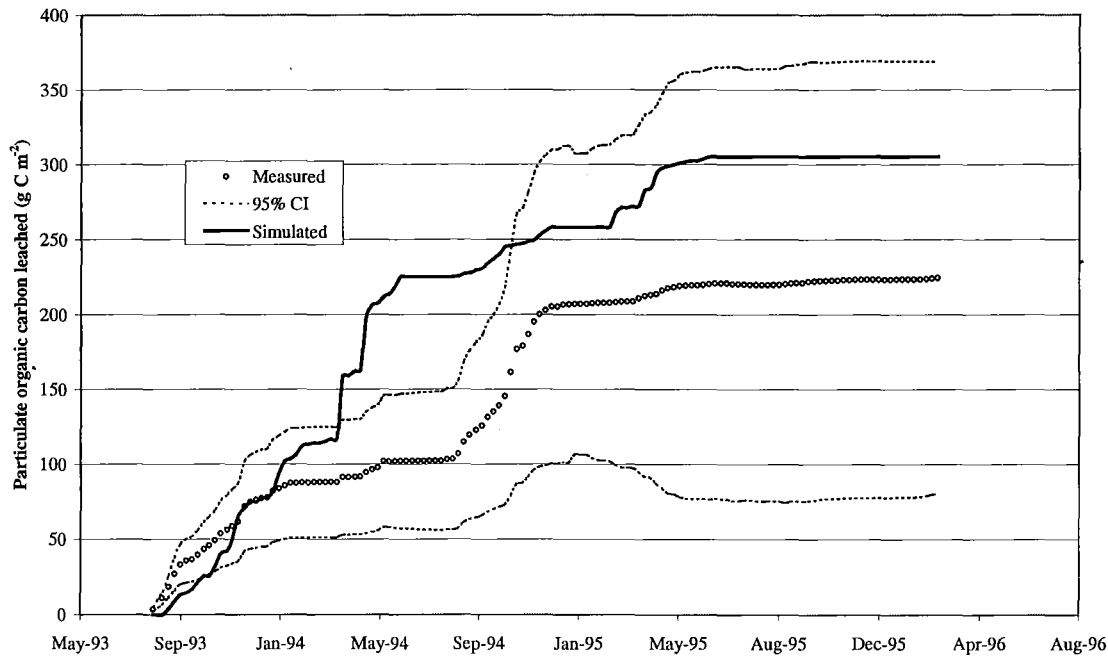


Figure 13.7 Simulated versus measured particulate organic C leaching for conventionally drained DFE-irrigated lysimeters from August 1993 to March 1996. Mean \pm 95% CI.

13.3.5 Dissolved organic C leaching

As is evident from Figure 13.8, the model over-estimated the leaching of dissolved organic C by a substantial amount, 440 g C m⁻² simulated compared to the measured amount of 110 g C m⁻². Though over-estimation occurred during the whole simulation period, it was particularly strong after the end of DFE irrigations in May 1995.

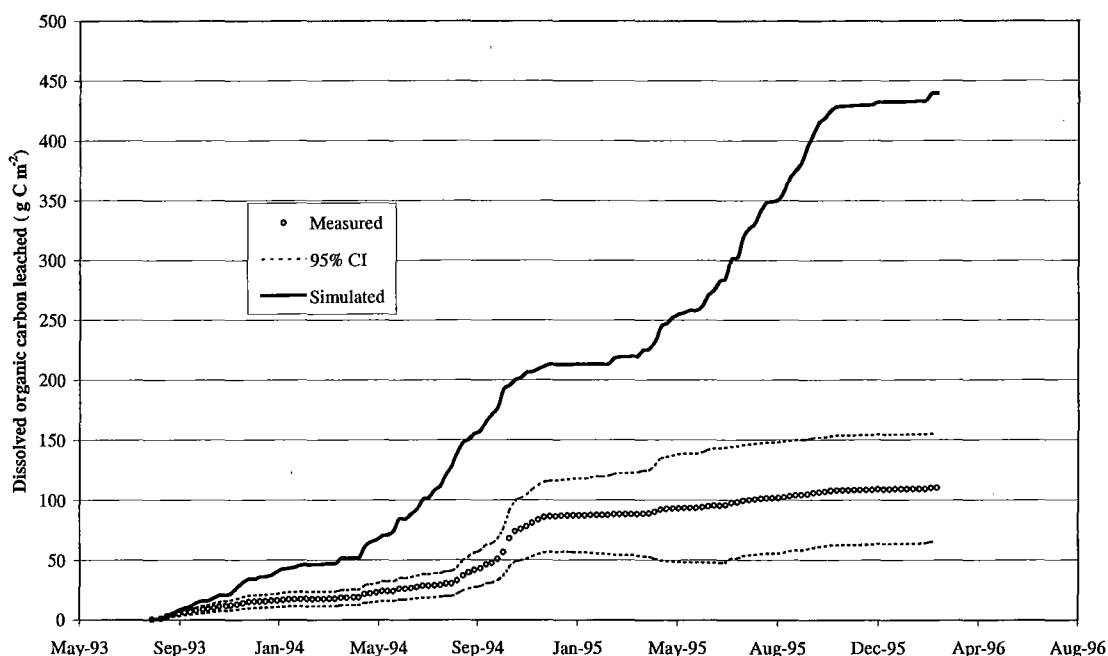


Figure 13.8 Simulated versus measured dissolved organic C leaching for conventionally drained DFE-irrigated lysimeters from August 1992 to March 1996. Mean \pm 95% CI.

13.4 Discussion

Three reasons could explain the simulated but not measured nitrate leaching during the first few months of the simulation, which disappeared when initial soil nitrate concentrations below the root zone were set to zero (data not shown). The initial soil nitrate concentrations may have been too high, denitrification in the subsoil may have been underestimated, or the N uptake by the pasture may have been higher than simulated. The last is the most likely reason, as higher N uptake than simulated was measured during this period (Figure 14.1). The agreement between simulated and measured $\text{NO}_3\text{-N}$ data would be extremely close if the initial leaching period was disregarded and the simulation would be within the 95% CI at all times.

Over-estimation of the plant N uptake (Figure 14.1) during the summer and autumn of 1994 could explain the lack of simulated $\text{NO}_3\text{-N}$ leaching during autumn 1994. Simulated soil inorganic N values (Figures 14.6 to 14.8) were also comparatively low, which is consistent with high plant uptake and a resulting lack of nitrate susceptible to leaching. A somewhat higher simulated than measured plant uptake would also account for the delay in simulated nitrate leaching in summer 1995 (Figure 14.1). The soil $\text{NO}_3\text{-N}$ (Figures 14.6 to 14.8) concentrations during the autumn 1995 were comparatively high, so the high $\text{NO}_3\text{-N}$ leaching simulated is not unreasonable.

Most of the measured $\text{NO}_3\text{-N}$ leaching occurred in the drainage produced from the wetting-up events in late summer and autumn. $\text{NO}_3\text{-N}$ leaching was not observed during winter when presumably high soil water contents inhibited nitrification. These observed dynamics, except for autumn 1994, were simulated by CaNS-Eff.

Considering that the leached nitrate was equivalent to less than 1% of the applied total N, the performance of CaNS-Eff is very encouraging in terms of both the simulated amounts and the dynamics.

Again, considering the small amounts of $\text{NH}_4\text{-N}$ actually leached, the model did exceptionally well at simulating this small amount. The simulated $\text{NH}_4\text{-N}$ leaching was under-estimated during effluent application, and subsequently over-estimated after the DFE irrigation had ceased (May 1995). There are three possible explanation for this behaviour. The maximum number of adsorption sites may have been over-estimated, the de-adsorption process is too slow or some form of non-reversible adsorption kinetics needs to be included in the model. As the total amount of $\text{NH}_4\text{-N}$ simulated and measured agreed very well, it would appear to be either the speed of de-adsorption kinetics, or the maximum amount adsorbed which needs to be addressed, as opposed to non-reversible kinetics. The maximum number of adsorption sites was estimated by the batch method (Chapter 6). This estimated value was then reduced to 33% of that determined, to account for not all of the potentially available soil adsorption sites being actually available under intact field conditions. This reduction may not have been sufficient and further work using column studies versus batch studies needs to be undertaken to ascertain the relationship between potentially and actually available adsorption sites.

CaNS-Eff over-estimated the amount of organic N leached in both the dissolved and particulate fractions. The particulate filtration sub-model, when applied to the total soil profile as opposed to the soil cores discussed in Chapter 5, over-estimated the amount of particulate N leached. This behaviour could result from inadequate filtration parameters used for the lower soil horizons. The lower soil horizons of the soil cores used for deriving the filtration parameters had been impermeable, as discussed in Chapter 5. The lower horizons in the lysimeters, however, contained cracks and wormholes that allowed water to move through these horizons. In the model, filtration parameters for these large macropores were chosen to allow all particulate material that reached these soil horizons to pass. This assumption may have resulted in an over-estimation of the amount of particulate N leached, as it is likely that some particulate material was filtered out during passage through these subsoil horizons.

As the comparison of the particulate and dissolved organic nitrogen curves has revealed, the dissolved fraction was responsible for the particularly high over-estimation of leached organic N during the post-irrigation period. This behaviour indicates problems with the adsorption/de-adsorption characteristics of dissolved organic N similar to that exhibited by NH_4 .

In spite of the permanent over-estimation of dissolved organic C, it is noteworthy that a high proportion of the simulated leaching of dissolved organic C occurred during the post-irrigation period, similar to the pattern of NH_4 and dissolved organic N. A possible contributing factor for the higher over-estimation of the leached dissolved organic C compared to the dissolved organic N is that root exudation produces dissolved C. If the rate of root exudation is too high, then excess dissolved C will be leached.

The over-estimation of the particulate C leached was primarily due to two major leaching events during the autumn of 1994. In both cases, the leaching occurred after extended dry periods when very little drainage occurred. During these dry periods, the size of the "free pool", which is the movable particulate C, continued to increase with DFE irrigation. As no drainage fluxes were occurring the particulate C could

not be leached from the soil profile. Upon re-wetting with a high drainage flux, this large “free pool” of particulate C was leached. As these events were not measured this behaviour appears to be unrealistic. The particulate filtration model may need to be modified, so that the size of the “free pool” is limited or more C is transferred into the “trapped pool” during extended dry periods. As the DFE at this time had very wide C:N ratios (30-45), this behaviour was more pronounced in the particulate C than the particulate N leaching data.

The particulate C concentration in the DFE was low during the 1994/95 DFE-irrigation season, when the simulated amount of particulate C leached was under-estimated. This may indicate that the filtration model does not simulate low concentrations of particulate material as well as it does larger concentrations.

13.5 Conclusions

Considering:

- the large amount of total N and C applied onto the lysimeters over the 42 months of operation (4 t ha^{-1} of N and 42 t ha^{-1} of C),
- the various forms of C and N in dissolved and particulate DFE, as well as in returned pasture,
- and that the parameters have not been calibrated,

the agreement in the dynamics and absolute amounts between the measured and the simulated values of leached C and N demonstrated that CaNS-Eff has the capability to describe the leaching of C and N from the application of an organic effluent onto the soil.

The model performed very well in terms of the non-adsorbed component of C and N. However, the de-adsorption behaviour of the isothermic pools needs to be improved. These improvements may include a non-reversible adsorption process, the de-adsorption kinetics being accelerated or the maximum amount of adsorption sites being determined from column studies as opposed to batch studies as used.

Chapter Fourteen

Pasture, microbial biomass and soil C and N response: simulated versus measured

The objective of this Chapter is to:

Compare the CaNS-Eff simulated pasture N, microbial biomass and soil C and N concentrations to the measured data in the conventionally drained DFE-irrigated lysimeters

14.1 Introduction

The complex model CaNS-Eff has been developed to simulate the response of the soil-plant system to the application of organic effluents. This Chapter reports on the performance of the model in terms of the plant growth, microbial biomass and soil C and N levels. Measured and simulated values from the conventionally drained treatment for:

- pasture N uptake
- microbial biomass in 3 topsoil layers
- total soil C and N concentrations in 3 topsoil layers

are compared in a verification exercise.

The simulated soil $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ concentrations in the 0-5, 5-10 and 10-20 cm soil layers are also presented, but no measured data are available for comparison.

The measured total soil C and N and microbial biomass data, determined across all DFE-irrigated treatments, are presented in Chapter 8.

14.2 Results

14.2.1 Pasture N

The simulated versus measured pasture N yield for the 39 pasture cuts made on the conventionally drained DFE-irrigated lysimeters treatment from September 1992 to February 1996 are given in Figure 14.1. Of the 39 cuts 21 simulated values are within the CI (54%), with 5 being too low and 13 being too high.

The statistical measures for evaluating the goodness of fit of the model (Whitmore, 1991) are presented in Table 14.1. The % variance (Greenwood, *et al.* 1985) was greater than 100%.

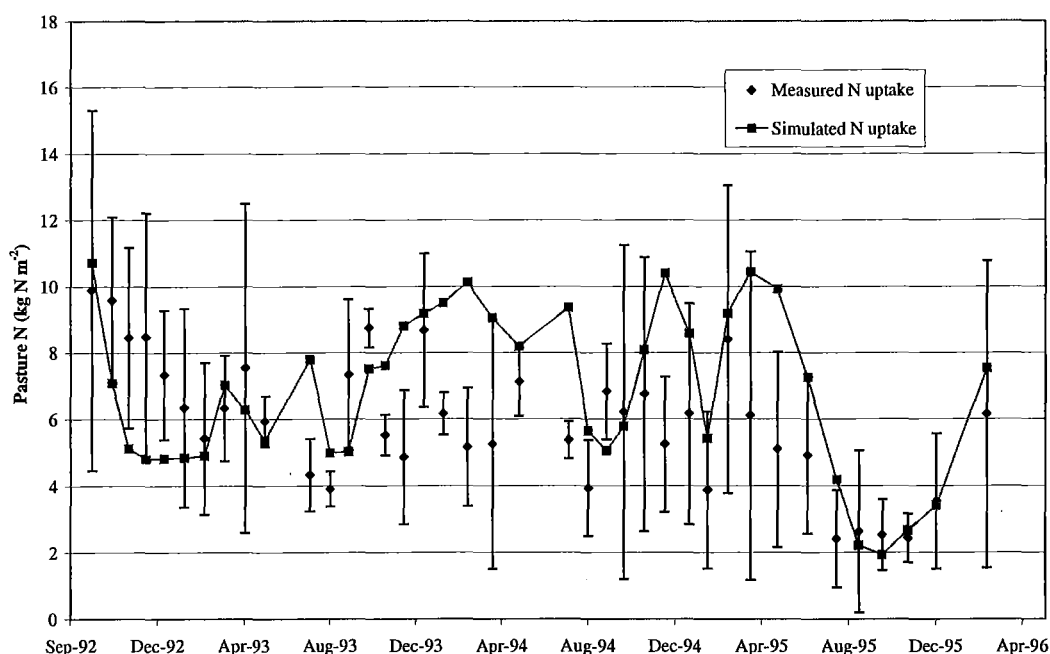


Figure 14.1 Simulated versus measured pasture N uptake for the conventionally drained DFE-irrigated lysimeters from September 1992 to February 1996. Mean \pm 95% CI.

Table 14.1 Statistical measures for goodness of fit of simulated versus measured pasture N uptake for the conventionally drained DFE-irrigated lysimeters.

Residual sum of squares (RSS)	Mean sum of squares due to pure error (MSE)	Mean square due to lack of fit (MSLOFIT)	Ratio of lack of fit/pure error (MSLOFIT/MSE)
718	1.23	15.9	12.9

14.2.2 Soil microbial biomass-C

The simulated amount and dynamics of the biomass-C in the 0-5 cm soil layer is in very good agreement with the measured data as shown in Figure 14.2. All simulated values, except for July 1994, are very close to the measured mean values and are well within the 95% CI.

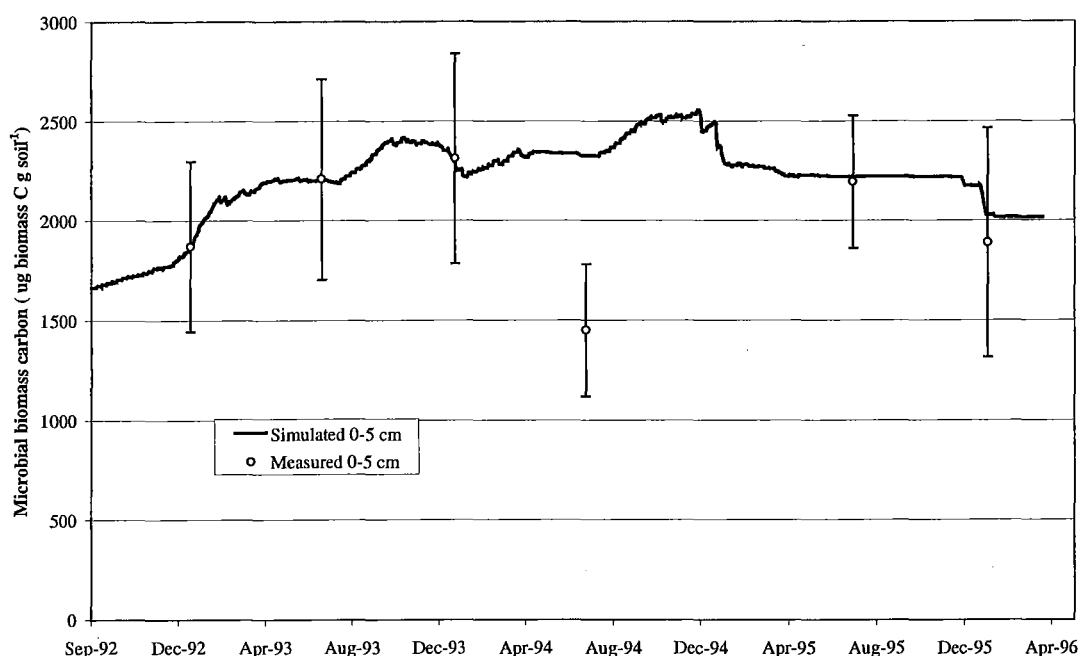


Figure 14.2 Simulated versus measured biomass-C in the 0-5 cm soil layer for the conventionally drained DFE-irrigated lysimeters from September 1992 to March 1996. Mean \pm 95% CI.

Good agreement between the simulated and the measured soil microbial biomass-C was also observed in the 5-10 and 10-20 cm soil layers, as shown in Figure 14.3. The simulated values were within the 95% CI in all cases in the 10-20 cm layer, and all but the July 1994 sampling in the 5-10 cm layer.

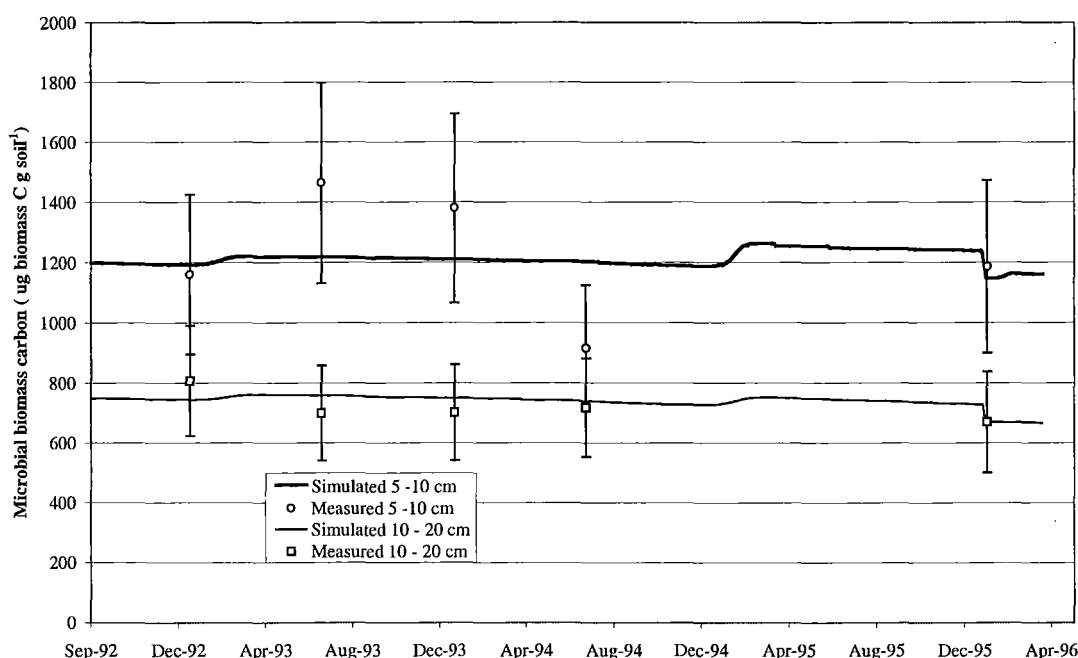


Figure 14.3 Simulated biomass-C versus measured data in the 5-10 and 10-20 cm soil layers for the conventionally drained DFE-irrigated lysimeters from September 1992 to March 1996. Mean \pm 95% CI.

14.2.3 Total soil C and N

The measured and simulated total soil C in the 0-5, 5-10 and 10-20 soil layers are given in Figure 14.4 with the corresponding data for the total N presented in Figure 14.5. CaNS-Eff simulated an accumulation of soil C and N from the DFE in the topsoil layer (0-5cm), but this accumulation was not measured. In the lower soil layers the simulated C agreed well with the measured data and while the N dynamics were in good agreement, the absolute values were under-estimated, indicating that the initial values were probably too low.

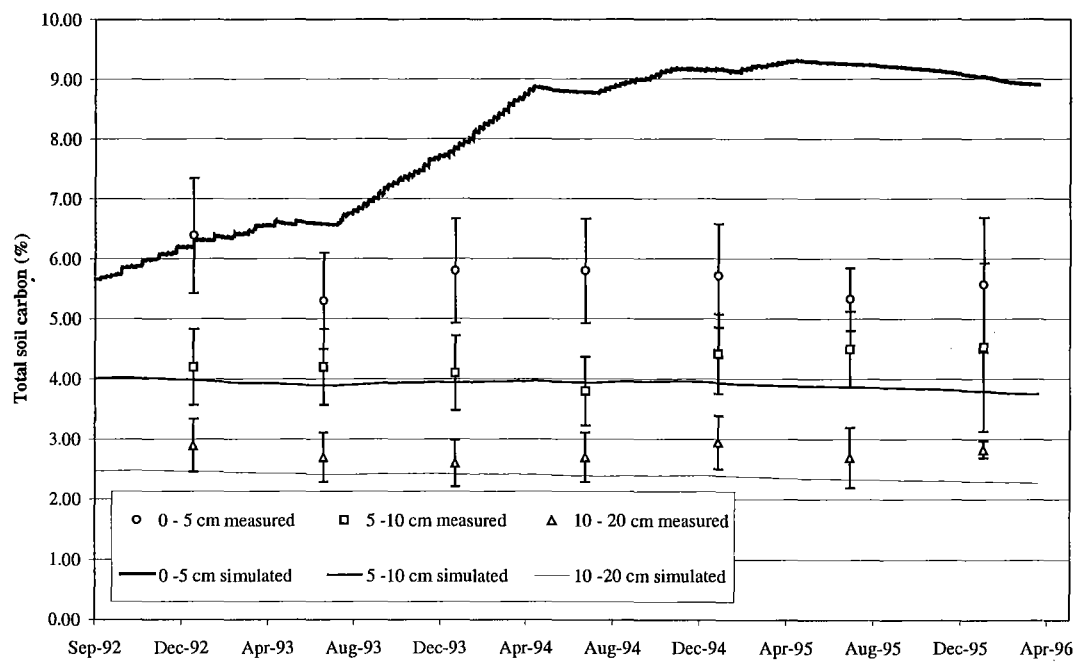


Figure 14.4 Simulated versus measured total soil C in the 5-10 and 10-20 cm soil layers for the conventionally drained DFE-irrigated lysimeters from September 1992 to March 1996. Mean \pm 95% CI.

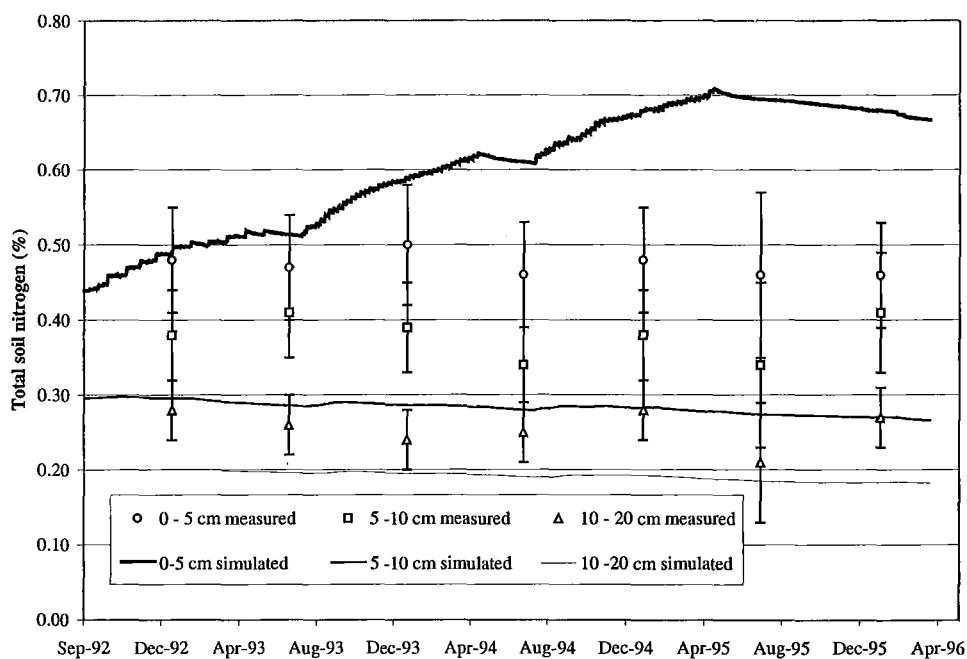


Figure 14.5 Simulated versus measured total soil N in the 0-5, 5-10 and 10-20 cm soil layers for the conventionally drained DFE-irrigated lysimeters from September 1992 to March 1996. Mean \pm 95% CI.

14.2.4 Soil inorganic N

Despite having no reliable measurements of soil $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ concentrations against which the simulated values can be compared, the soil inorganic N levels are still reported, as they are considered to be key outputs from any C and N simulation model. Figures 14.6 to 14.8 present the soil inorganic N data for the 0-5, 5-10 and 10-20 cm soil layers respectively.

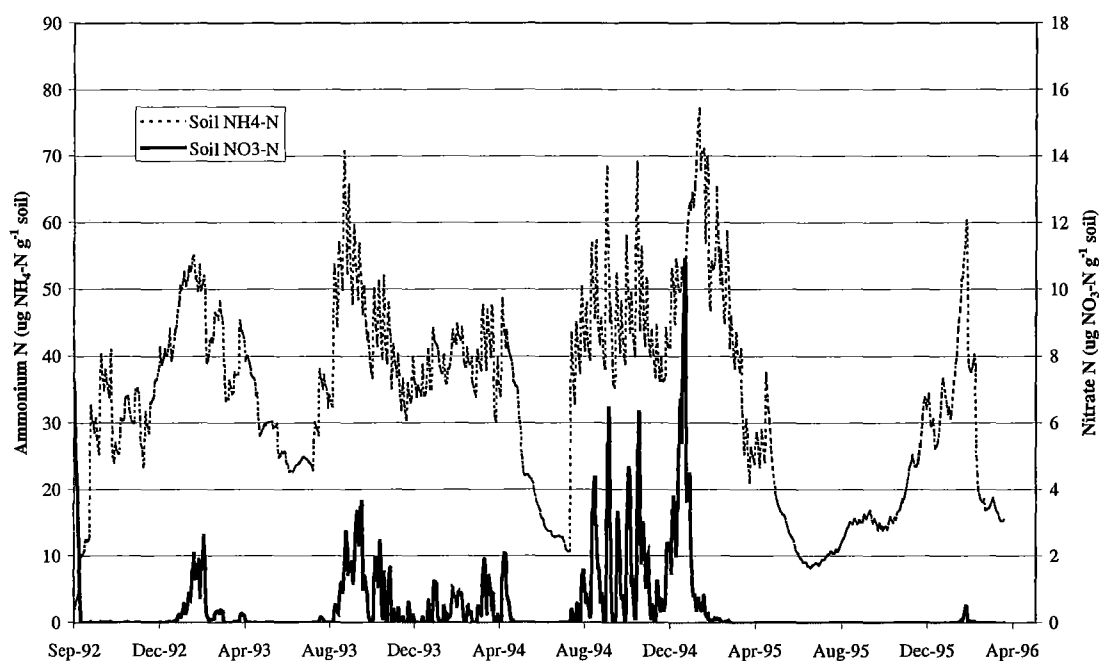


Figure 14.6 Simulated soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ concentrations in the 0-5 cm soil layer for the conventionally drained DFE-irrigated lysimeters from September 1992 to March 1996. Note that the $\text{NO}_3\text{-N}$ scale is on the secondary Y axis.

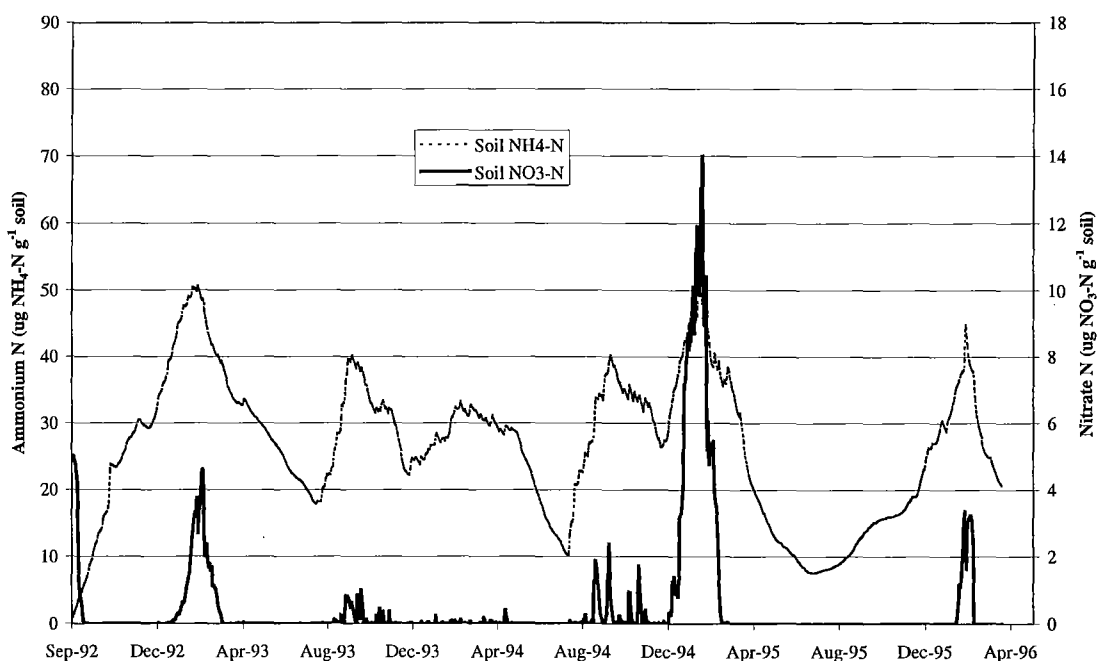


Figure 14.7 Simulated soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ concentrations in the 5-10 cm soil layer for the conventionally drained DFE-irrigated lysimeters from September 1992 to March 1996. Note that the $\text{NO}_3\text{-N}$ scale is on the secondary Y axis.

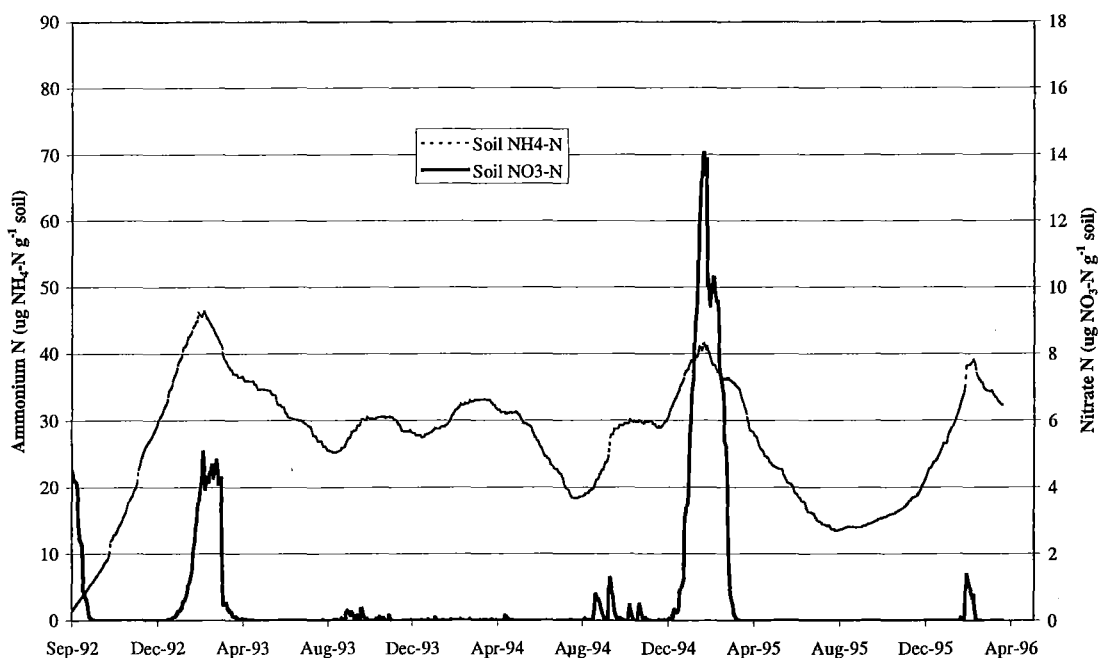


Figure 14.8 Simulated soil $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ concentrations in the 10-20 cm soil layer for the conventionally drained DFE-irrigated lysimeters from September 1992 to March 1996. Note that the $\text{NO}_3\text{-N}$ scale is on the secondary Y axis.

14.3 Discussion

The pasture N uptake simulated using the uncalibrated CaNS-Eff over the 42-month period was generally in good agreement with the measured values, except for the twelve-month period from August 1993 to August 1994 (Figure 14.1). This is an important result as plant uptake is the major and most desirable pathway for N removal from an effluent treatment site. During the 12-month period from August 1993 to 1994, the model tended to over-estimate the rather erratically measured pasture N uptake. Possible reasons for this over-estimation are: a too high growth of the pasture C simulated by the GRASS sub-model, too high Michaelis-Menten root N uptake kinetic parameters, or a too low target C:N ratio for the pasture. The available data do not allow more specific identification of the likely cause of the temporary over-estimation during this period.

The simulated pasture N uptake over the 15-month period from December 1994 to March 1996 was in very good agreement with the measured data, especially considering the rather dynamic nature of the measurements. From the perspective of managing an effluent treatment system, the simulated pasture N uptake is the most important component in the plant model. Additionally, once the plant model was checked thoroughly, it could also be used in scenario studies to optimise the quantity and quality of pasture produced on land treatment sites.

The exceptionally good simulation of the microbial biomass dynamics and amounts by CaNS-Eff is very promising, as the soil microbial biomass is the key transformation station for organic materials. Even though the errors associated with the biomass measurements were large, CaNS-Eff simulated values that were very close to the measured mean data. The biomass measurement of July 1994 appeared to be an outlier, as this value was very low in comparison to other measured values and there was no change in the

management of the lysimeters that could account for the decrease. The model simulated correctly the more dynamic response of the microbial biomass in the top layer compared to the subsoil layers. Considering that the biomass parameters have not been calibrated, the size of the microbial biomass population is not bounded, and that their activity is based on substrate supply, the close results between simulated and measured are very encouraging.

Excepting the topsoil layer, CaNS-Eff simulated closely the measured total soil C and its dynamics. The model simulated an accumulation of C in the topsoil layer that was not measured. The largest period of accumulation in this layer was during the 1993/94 DFE-irrigation season, which is consistent with the high application of nearly 22 tonnes of C ha⁻¹ over this period. A larger accumulation was simulated in the 1992/93 irrigation season than in 1994/95, despite approximately the same amount of total C being applied in both seasons. The likely reason for the higher accumulation in 1992/93 is the different microbial availability of the returned clippings. The accumulation of C in the topsoil layer appears to represent more closely our understanding of the system, where 42 tonnes of C ha⁻¹ were applied and only 30% respired (Chapter 3) as CO₂. This must result in an accumulation in the soil profile. This discrepancy between the measured data and the simulated result is difficult to explain.

While the simulated total soil N dynamics in the lower layers were in good agreement with the measured data, the absolute values differed slightly. The discrepancy between them was evident from the start of the model, which indicates that the initial values for total soil N were too low. In the same manner that C accumulation was predicted, N was also predicted to accumulate in the topsoil layer. The amount of N accumulation was similar in each irrigation year, reflecting the similar N loadings.

For grazed pasture, the simulated soil NH₄-N levels appear to be very high. However, it needs to be considered that a weekly application of the NH₄-N in DFE when uniformly distributed over the 0-10 cm soil depth can represent an increase in soil NH₄-N levels of 22 µg NH₄-N g soil⁻¹. Elevated levels of ammonium are therefore to be expected. Nitrification may also have been impeded by the lack of aeration in the lysimeters. This poor soil aeration, as seen in the high WFPS data (Chapter 12), is due to the regular weekly application of DFE onto the clay soil. The high adsorption of NH₄ onto the soil also means that much of the NH₄-N present is unavailable for plant or microbial processes, and only as the pore water concentration decreases can the NH₄-N de-adsorb and adsorbed soil concentration decrease. As discussed in Chapter 6, the maximum number of adsorption sites for NH₄-N was based on batch trials. These trials determine the maximum number of potentially available adsorption sites. As discussed in Chapter 13 in relation to NH₄ leaching, this maximum number of potentially available sites may be too high. Any reduction in the maximum number of sites would also see a reduction in the simulated soil NH₄ concentrations.

The dynamics of the soil nitrate response with increasing levels during the autumn periods appear reasonable. This is encouraging as the nitrification process is modelled on the microbial dynamics of the nitrifier population and not directly on the soil NH₄-N concentration. It may have been expected that the soil nitrate levels may have been higher at other times through the year. However, as very little NO₃-N was in fact leached, the low simulated levels are consistent with this measured leaching result. As expected, the nitrate dynamics reflects that of the “substrate NH₄” but at a much lower level.

The post-DFE irrigation period showed an increase in soil $\text{NH}_4\text{-N}$ levels from the mineralisation of soil organic matter, residual effluent organic matter and dying microbial biomass. This is supported by the increase in measured pasture response that occurred over the same period. The peak occurring in January 1996 in all three soil layers coincides with the correctly simulated death of microbial biomass. During this post-DFE irrigation period, the increase in the soil $\text{NH}_4\text{-N}$ levels reflects the increased microbial activity due to higher soil temperatures.

14.4 Conclusions

The ratio of the MSLOFIT/MSE for the simulated pasture yields indicates that the error in the lack of fit of the model was approximately 15 times greater than the pure error in the measured data, which suggests, as does the high % variance, that the pasture sub-model within CaNS-Eff could be improved.

It is recommended that column studies be used to try and ascertain a better estimate of the actual maximum number of adsorption sites that intact soils have available to a solution flowing through the core.

Overall, the uncalibrated performance of the CaNS-Eff model was satisfactory in terms of the simulation of the plant and soil processes and the model warrants further testing and development.

14.5 References

- Greenwood, D. J., Neeteson, J.J. & Draycott, A. 1985, Response of potatoes to N fertilizer: Dynamic model, *Plant and Soil* **85**: 185-203.
- Whitmore, A.P. 1991, A method for assessing the goodness of computer simulation of soil processes, *Journal of Soil Science* **42**: 289-99.

Chapter Fifteen

Summary of thesis

15.1 Introduction

The dairy sector is New Zealand's largest industry, and one of its major effluent streams comes from the cleaning of the milking dairy and associated holding yards on the farm. The resulting very dilute organic effluent, called dairy farm effluent (DFE), consists of a mixture of urine and faeces combined with wash-down water. Regulatory bodies have promoted land application of DFE as their preferred treatment option and the adoption of this technology has been relatively rapid. However, application of effluents containing N must be treated cautiously. The risk of further increasing already elevated nitrate levels in intensively farmed areas through inappropriately managed DFE-irrigation needs to be minimised.

The allowable annual loading rate for DFE, as defined in statutory regional plans for various regions of New Zealand, ranges from 100 to 300 kg N ha⁻¹ yr⁻¹. These rates are largely based on annual N balance calculations, comparing N inputs to outputs from the farming system, which include an allowable leaching loss. Little information is available, however, to assess the effects that these loading rates have on the receiving environment. It is this need, to understand the fate of land-applied DFE and develop a tool to describe the process, that is addressed in this thesis. This goal is met through laboratory experiments and field studies that have resulted in the development and testing of the simulation model CaNS-Eff, capable of describing the fate of DFE applied onto land.

15.2 Goal and objectives of the study

The overall goal of the research reported in this thesis was to:

Understand the fate of land-applied DFE and develop a tool capable of simulating this treatment option.

This goal was met through the following objectives:

1. Identify and understand the key processes that control the fate of DFE irrigated onto soil.
2. Develop a mathematical description for these processes and integrate them into a holistic model.
3. Determine parameters that are suitable for use in the mathematical descriptions.
4. Develop data sets that can be used to test the simulation model.
5. Check the adequacy of the model by comparing the simulated values against measured data.

Four separate facets of work were undertaken to meet these objectives.

1. Laboratory process studies have been completed to:

- Obtain an understanding of the soil biological processes involved when organic material is added to the soil.
- Determine parameters that describe the response of microbial populations when organic material is added to soil.
- Describe and parameterise the transport of the particulate fraction of DFE in soil.
- Describe the non-equilibrium adsorption kinetics involved in the addition of DFE to soil.

2. Field lysimeter studies were used to:

- Identify key processes in the fate of organic effluent irrigated onto soils under field conditions.
- Provide data sets against which the simulation model could be tested.

3. The development and parameterisation of a comprehensive simulation model (CaNS-Eff) describing the fate of organic effluent added to soil.

4. The comparison of simulated values from CaNS-Eff with measured data to ascertain the adequacy of the model to describe the fate of DFE irrigated onto soil.

15.3 Summary of laboratory results

The microbially mediated net N mineralisation from DFE takes a central role in the turnover of DFE, as the total N in DFE is dominated by organic N. The relevant parameters in this process were determined in a soil incubation study (Chapter 3) where concomitantly net C and N mineralisation were measured as well as microbial dynamics, after the addition of DFE to soil. This study showed that at the standard farm loading rate of 68 kg N ha⁻¹, the net C mineralisation from DFE was finished 13 days after application, and represented 30% of the applied C with no net N mineralisation being measured by the end of the experiment (Day 113). At a higher loading rate of 345 kg N ha⁻¹, the extent and dynamics of DFE turnover differed, with 48% of the applied C being mineralised by Day 50, and 14% of the organic N being mineralised by Day 113. The higher loading rate tended to support a higher microbial-C concentration than the control over the 113 days, while the standard rate had only a minor effect. The soluble fraction of DFE appeared to have a microbial availability similar to that of glucose. However, the microbial biomass could use the compounds contained in the soluble DFE immediately without adaptation, unlike glucose, which showed high mineralisation rates after a short lag phase.

From the low and gradually changing respiration rate measured from DFE, it appeared that DFE is more like a semi-continuous substrate supply to the microbial biomass than a pulse of highly available substrate

(glucose, soluble DFE). This pattern reflected the complex nature and broad range of C compounds in DFE, which are being successively mineralised. Repeated application of DFE will gradually enhance the mineralisable fraction of the total soil organic N, and in the long-term, increase net N mineralisation. As a consequence, the permitted DFE loading rates should not be based on the impact of DFE on inorganic N pools directly following a single application, but on the long-term effects of regular DFE applications.

To address the lack of data on the fate of faecal-N in DFE, a ^{15}N -labelled faecal DFE component was applied onto intact soil cores with pasture grown on them under two different water treatments (Chapter 4). At the end of 255 days, approximately 2% of the applied faecal ^{15}N had been leached, 11% was in plant material, 11% was still as effluent on the surface, and 40% was in the soil (39% as organic N). Unmeasured gaseous losses and physical losses from the soil surface of the cores supposedly account for the remaining ^{15}N (approximately 36%). It was not possible to directly translate the measured ^{15}N recoveries into the turnover of the total faecal-N in the DFE, as this calculation relies on the small, labelled portion directly reflecting the dynamics of the larger unlabelled portion. This requirement was not met for two reasons: firstly, the organic fraction of the DFE had a higher enrichment of ^{15}N than the ammonium fraction; and secondly, the smaller sized organic fractions in DFE had a lower enrichment than the larger sized material. Consequently, disproportionally more of the ^{15}N than of the unlabelled N was filtered out on the soil surface. By making a simplifying assumption about the enrichment of the ^{15}N in the DFE that infiltrated the soil, the contribution from DFE-N to all plant-available N fractions including soil inorganic N was estimated to have been approximately 11% of the applied DFE-N.

As field studies have shown that on some soils between 60 and 70% of the N and C leached from the application of DFE was particulate, the simulation model developed to simulate the fate of land-applied DFE needed to include a description of this process. The filtration behaviour of four soil horizons was measured by characterising the size of C material in a DFE, applying this DFE onto intact soil cores, and collecting and analysing the resulting leachate using the same size characterisation (Chapter 5). After two water flushes, an average of 34% of the applied DFE-C was leached through the top 0-50 mm soil cores, with a corresponding amount of 27% being leached from the 50-150 mm soil cores. Only one of the subsoil cores tested produced C leachate, and this was through bypass flow. Most of the C leaching occurred during the initial DFE application onto the soil. To describe this transport and leaching of particulate C a simulation sub-model, used in CaNS-Eff, was developed and parameterised. It describes the movement of the effluent in terms of filtering and trapping the C within a soil horizon and then subsequently washing it out with flow events. The parameterised model was capable of describing the observed leaching behaviour.

When DFE is irrigated onto soil, some of the compounds contained in DFE adsorb onto the soil and are removed from the infiltrating effluent. To describe this process and the resulting distribution of the adsorbed fractions of DFE following irrigation, a non-equilibrium adsorption equation was derived and parameterised using batch studies (Chapter 6). This work was completed for four soil horizons for NH_4 and the dissolved organic C and N fractions of DFE.

15.4 Summary of field data

To evaluate the sustainability of DFE application onto land and provide a data set against which the adequacy of CaNS-Eff could be tested, all C and N applied, leached, removed by pasture or accumulated in the soil, was measured over four years using replicated field lysimeters. At the high DFE loading rate used, the total soil C and N, pH and the microbial biomass (Chapter 8) all increased at different rates. The long-term sustainability of the application of DFE can only be maintained when the supply of inorganic N is matched by the demand of the pasture. In pastures that contain clover, increased mineralisation of gradually accumulating organic N may be offset by reduced N-fixation.

In the third year of operation, 1554 kg ha⁻¹ of DFE-N was applied onto the controlled drainage lysimeters (Chapter 7). The main removal mechanism was pasture uptake, with the DFE treatments removing 700 kg N ha⁻¹ through pasture and the water irrigated treatment removing 390 kg N ha⁻¹. On average, 193 kg N ha⁻¹ was leached from the DFE treatments, with 80% of this being organic N. The amount of nitrate leached decreased as the soil water content increased through the use of controlled drainage.

The measured bromide leaching from an irrigation event showed that on average 18% of the bromide bypassed the soil matrix and was leached in the initial drainage event. This bypass mechanism accounted for the high amount of organic N leached under DFE-irrigation. The soil water status, application rate, and history of effluent application will all influence the amount of bypass flow produced from an initial irrigation event. However, the level of controlled drainage had no effect. The peak concentration of bromide is lower with an increased saturation zone in the soil profile. Also, as the zone of saturation increases, the recovery of the dissolved fractions from the immobile zone is earlier as there is more opportunity for diffusion to occur from the increased immobile zone.

To select an appropriate hydrology sub-model to use within CaNS-Eff, the simulated drainage volumes and water table heights were compared to the measured data across all drainage conditions over four years using two different modelling approaches (Chapter 9). The two models were a simple water balance model, DRAINMOD (Skaggs, 1980), and a solution to Richards' equation, SWIM (Ross, 1990). While DRAINMOD was capable of describing controlled drainage, SWIM needed to be modified. Both models gave excellent estimation of the total amount of drainage, with the simulated cumulative drainage being between 93% and 116% of the observed values. In all treatments, DRAINMOD tended to over-estimate the total drainage whereas SWIM tended to under-estimate. The greatest errors in drainage volume were associated with rain events over the summer and autumn, when antecedent soil conditions were driest. Both models could simulate the height of the water table relatively well, but SWIM tended to track the measured values better than DRAINMOD. When soil water and interlayer fluxes are required at small time steps, such as during infiltration under DFE-irrigation, SWIM's more mechanistic approach offered more flexibility and consequently was the sub-model selected to use within CaNS-Eff.

15.5 Summary of model development

The complex simulation model of the soil-plant-microbial system, CaNS-Eff, has been developed to describe the transport and transformations of C and N components in effluents applied onto the soil (Chapter 10). The soil profile was divided into layers to describe the microbial, chemical and/or physical boundaries that are considered to exist within the soil. The model simulates the transport, adsorption and filtration of both dissolved and particulate components of an effluent. Soil water, that can carry both dissolved and particulate material, moves between the computational layers. The soil matrix is further divided into immobile (micropore) and mobile (mesopore) flow domains, with convective flow of solutes occurring in the mobile fraction only. The solute and water infiltrating into a new mesopore domain mixes with the water and solute that are currently in that domain, and with the next flux event are available to move down the soil profile. This mixing effectively introduces dispersion into the model. Obviously, with this implementation the concentrations of dissolved materials will be different in the two flow domains. Diffusion is considered to occur between the micropore and mesopore flow domains within a soil layer, allowing dissolved material to move into the immobile zone. Diffusion is also considered to occur between the two micropore and mesopore domains in adjacent soil layers. CaNS-Eff is designed to allow various soil water flow sub-models to be used to provide interlayer fluxes and soil water contents on the same spatial basis as the C and N transformation process model.

The microbial availability of the various organic fractions within the soil system are described by availability spectra of multiple first-order decay functions. The simulation of microbial dynamics is based on actual consumption of available C by the three microbial biomass populations: heterotrophs, nitrifiers and denitrifiers. The denitrifiers are considered to be identical to the heterotrophs, except that denitrifiers can use NO_3 if there is insufficient oxygen for oxidising their allocated C. The nitrifiers are a special case, as their energy requirement for growth and respiration is met by the nitrification of NH_4 . The microbial activity or respiration level of a population is controlled by the amount of C that is available to that population. The respiration rate can vary between low level maintenance requirements, when very little substrate is available, to higher levels for an actively growing population when excess substrate is available. An algorithm based on uptake kinetics and total substrate requirements is used to solve the problem of competition between microbial populations and/or plant requirements for substrate materials such as $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, available C and O_2 . Microbial death can occur through either substrate and/or oxygen shortfall with differing simulated responses depending on the cause of the stress.

The plant component is described as both above- and below-ground fractions of a ryegrass-clover pasture. The C:N ratios of each of the fractions are allowed to vary within limits around seasonally optimal values. The pasture growth model based on GRASS (Baars and Rollo, 1993) uses soil moisture, soil temperature, solar radiation and current plant biomass levels to predict the potential plant growth rate. This potential growth can only be achieved provided sufficient foliage N is available to satisfy the demand of photosynthetic carbon growth. Translocation between the foliage and the roots of both C and N ensures that the two plant fractions maintain optimal C:N ratios as well as a realistic foliage to root ratio. The percentage of clover N that is fixed from the atmosphere is based on the given percentage of clover in the

pasture and the root zone water content and nitrate concentrations. Root death and exudation provide input of microbially available C to the soil.

There are two soil atmosphere sub-models implemented in CaNS-Eff, a simple sub-model where oxygen concentration is related to soil tension, and a more mechanistic approach which simulates the concentration and movement of CO₂, N₂ and O₂, based on pressure equalisation and diffusion through the soil column.

The parameter set used with CaNS-Eff to simulate the fate of DFE applied onto conventionally drained lysimeters over three years with a subsequent 10-month non-irrigation period was derived from field measurements, laboratory studies, experimental literature data and published model studies (Chapters 9 and 11). As no systematic calibration exercise was undertaken to optimise these parameters, the data set should be considered as “initial best estimates” and not as a calibrated data set on which a validation exercise of CaNS-Eff could be based.

15.6 Summary of the comparisons of the simulated with measured data

Over the 42 months of simulation, the cumulative drainage from CaNS-Eff for the conventionally drained DFE-irrigated lysimeter was always within the 95% CI of the measured mean value (Chapter 12). The total simulated drainage volume at the end of this period was within 0.5% of the measured value of 3537 mm. On the basis of individual drainage bulking periods, CaNS-Eff was able to explain 92% of the variation in the measured drainage volumes. The accuracy of the simulated water filled pore space (WFPS) was better than that of the drainage volume, with an average of 70% of the simulated WFPS values being within the 95% CI for the three soil layers investigated. In contrast, only 44% of the individual drainage volumes were within the 95% CI. Overall the hydrological component of CaNS-Eff, which is based on the SWIM model (Ross, 1990), could be considered as satisfactory for the purposes of predicting the soil water status and drainage volume from the conventionally drained lysimeter treatment.

The simulated cumulative nitrate leaching of 4.7 g NO₃-N m⁻² over the 42 months of lysimeter operation was in good agreement with the measured amount of 3.0 (± 2.7) g NO₃-N m⁻² (Chapter 13). Similarly, the total simulated ammonium leaching of 2.7 g NH₄-N m⁻² was very close to the measured amount of 2.5 (± 1.35) g NH₄-N m⁻². However, the dynamics were not as close to the measured response as with the nitrate leaching. The amount of simulated organic N leached was approximately double that measured, most of the difference originating from the simulated de-adsorption of the dissolved fraction of organic N during the 10-month period after the final DFE-irrigation. The 305 g C m⁻² of simulated particulate C leached was close to the measured amount of 224 g C m⁻² over the 31 months of simulation. The dissolved C fraction was substantially over-estimated. Taking into account that the parameter set is based on “initial best estimates”, as opposed to calibrated parameters, the agreement in the dynamics and the absolute amounts between the measured and simulated values of leached C and N demonstrated that CaNS-Eff contains an adequate description of the leaching processes following DFE-irrigation onto the soil. There was good agreement in the non-adsorbed and particulate fractions of the leached C and N in DFE. The isothermic behaviour of the adsorbed pools indicated that a non-reversible component needs to be introduced or the dynamics of the adsorption/de-adsorption need to be improved.

The simulated pasture N production was in reasonable agreement with the measured data, with 21 (54%) of the 39 cuts being within the 95% CI; 5 being too low and 13 being too high (Chapter 14). The simulated dynamics and amounts of microbial biomass in the 0-5, 5-10 and 10-20 cm soil layers were in exceptionally good agreement with the measured data. This is an important result as the microbial biomass is the key transformation station for organic materials. Excepting the topsoil layer, the simulated total C and N dynamics were close to the measured values. While the total soil N dynamics of the lower layers were in good agreement the absolute amounts differed slightly, indicating an error in the initial values. The model simulated an accumulation of C and N in the topsoil layer that was expected, but not measured. Although no measured data were available to compare the dynamics and amounts of the soil nitrate and ammonium, the simulated values appear realistic for an effluent treatment site and are consistent with measured pasture data.

Considering:

- the large amount of total N and C applied onto the lysimeters over the 42 months of operation (4 t ha^{-1} of N and 42 t ha^{-1} of C),
- the various forms of C and N in dissolved and particulate DFE, as well as in returned pasture,
- and that the parameters have not been calibrated,

the simulated values from CaNS-Eff compared satisfactorily to the measured data. The steps necessary to improve and develop CaNS-Eff further are discussed in Section 15.7.2 below.

15.7 Further work

Some recommendations for future research as a result of this study include:

15.7.1 Process studies

- For verification of the theoretical relationship between C and N mineralisation after the addition of organic materials to the soil, better measurement techniques for the total and active amounts of soil microbial biomass-C and -N are required.
- The reasons for soil microbial responses varying with different loading rates of the same organic substrate need to be determined.
- To enable the use of isotopic labelling of organic material, the different enrichment of various fractions needs to be investigated. Strategies for the separation of these various components need to be developed so that conclusive results can be obtained from laboratory or field studies.
- The relationship between pore size distribution of a soil and its filtration performance of particulate material in effluent needs to be developed, so that filtration performance can be estimated from soil retention data.

15.7.2 *Model development*

- The relationship between adsorption parameters derived from batch studies compared to those from column studies needs to be investigated. Protocols for the measurement of the appropriate adsorption parameters to use with CaNS-Eff need to be developed.
- The difficulty in determining parameters for the availability bins used in CaNS-Eff confirms that a standardised carbon fractionation scheme for describing the microbial availability of the various C substrates needs to be urgently developed.
- CaNS-Eff needs improvement in its description of adsorption kinetics. A full sensitivity analysis of the parameters used in the model should then be completed. The critical parameters identified should then be calibrated and a thorough validation exercise using an independent data set undertaken. The validation exercise may either indicate further development work is necessary or if good agreement between simulated and measured data is achieved, then confidence can be obtained in CaNS-Eff's performance.

15.8 References

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